Abstracts of the Papers Published in Other Journals by the Staff Members of the Institute During 1966 (Special Issue on Polymer Chemistry, IV)

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Nuclear Physics and Chemistry

Effect of Chemical State on the Decay Constant of U^{235m}. Hiromasa Mazaki and Sakae Shimizu. *Physical Review* 148, 1161 (1966). —Experimental investigation of the influence of chemical forms on the decay constant of U^{235m} has been performed. The U^{235m} atoms from a very thin Pu^{239} source were collected by the recoil method on platinum, carbon, and silicon plates in a pure argon atmosphere. Applying the differential method with two identical, specially designed 12-stage secondary electron multipliers, emission rates of the internal-conversion electrons of very weak energy from the isomer in different chemical states have been compared. Stability and sensitivity of the whole measuring system have been checked using C^{14} and metallic U^{235m} sources. We used metallic uranium (U) and uranium atoms slightly diffused into carbon (UC) or silicon (USi) base for the different chemical states. The results are: $\lambda(U)-\lambda(UC)=(3.18\pm0.50)\times10^{-3}\lambda(U)$, $\lambda(U)-\lambda(USi)=(2.21\pm0.36)\times10^{-3}\lambda(U)$, and $\lambda(USi)-\lambda(UC)=(0.97\pm0.43)\times10^{-3}\lambda(USi)$. Errors are standard deviations. We also determined the half-life of U^{235m} to be $T_{1/2}=26.05\pm0.05$ min. by using a low-background 2π gas-flow counter. Furthermore, diffusion of the isomer into the base materials, carbon and silicon, was investigated in some detail.

The Transition Energy of $^{235}U^{m}$. Hiromasa Mazaki and Sakae Shimizu. *Physics Letters* 23, 137 (1966). —The transition energy of the isomeric state (τ 1/2=26 min) in ^{235}U has been determined using a specially designed 12-stage secondary electron multiplier. Applying the retarding method with this multiplier, the transition energy of this state was determined as to be 30±3eV.

Continuous Energy Spectra of Protons and Alpha Particles Emitted by the Deuteron and Alpha Particle Reaction. Kiyoji Fukunaga, Hitoshi Nakamura, Tetsumi Tanabe, Kazuhiko Hosono and Seishi Matsuki. *Journal of the Physical Society of Japan* 21, No. 12 (1966).—Continuous energy spectra of protons and alpha particles have been studied in the deuteron-alpha particle scattering at the incident deuteron energy of 14.2 MeV. In the energy spectra of protons, the evidence for a final state resonance in the neutron and alpha particle system has been obtained and the energy spectrum is compared with the theory of final state interaction. There is a good agreement between the experiment and the theory. The angular dependence of the cross sections at peaks shows a stripping like feature. The energy spectrum of the alpha particles at the higher energy is mainly affected by the effect of the final state interaction of the triplet S state in the neutron and proton system. The angular dependence of these alpha particles shows a forward peak in the laboratory system and it can be explained by an exchange process.

Elastic and Inelastic Scattering of Deuterons form Be^9, C^{12}, N^{14} and O^{16} at 14 MeV. Dai-Ca Nguyen. *Journal of the Physical Society of Japan* **21**, No. 12 (1966).—Angular distributions of the elastic and of the inelastic scattering of deuterons from Be^9, C^{12}, N^{14} and O^{16} were measured with a broad range magnetic spectrograph followed by nuclear emulsion plates at intervals of 5° between 10° and 80° in the laboratory system. Deuterons leading to the 2.31 MeV T=1 state of N^{14} were not distinguished from the background so that the violation of the isobaric spin selection rule was not observed. For Be^9, the 2.43 MeV 5/2 rotational state was excited more strongly than the neighboring states. The 4.43 MeV rotational state of C^{12} was also strongly excited. In the case of O^{16}, the 6.14 MeV 3^- octupole vibrational state was resolved from the 6.06 MeV 0^+ state and was found to be excited more strongly than the 6.06 MeV 0^+ state and also than the 6.92 MeV 2^+ and 7.12 MeV 1^- states. Comparing with the results from the inelastic scattering of protons and of alpha particles, the present results indicate that collective states which are excited strongly by protons and by alpha particles, are also excited strongly by deuterons. Experimental angular distributions were fitted with the predictions of the nuclear interaction theory of Huby and Newns and of the diffraction theory of Dar and with the results from the DWBA analysis.

On the 3^- State in ^{28}Si and ^{24}Mg. J. Kokame K. Fukunaga and H. Nakamura. *Physics Letters* **20**, 672 (1966).—By DWBA analysis of α-particle inelastic scattering on ^{28}Si at E_α=28.4 MeV, the collective enhancement of the 3^-level at 6.88 MeV is determined as $B(E3)/B(E3)_{s.p.}$=6.1. In ^{24}Mg, a 3^- level is located at 8.4 MeV with an enhancement factor of 2.9.

Analytical Chemistry

The Coprecipitation Behavior of Rare Earth Elements with Calcium Oxalate upon Precipitation from a Homogeneous System. Masakazu Matsui. *Bulletin of the Chemical Society of Japan* **39**, 1114 (1966).—The effects of the pH value, the concentration of organic acid and several other variables upon the distribution coefficient were studied for the coprecipitation process of the calcium-lanthanide oxalate system. The logarithmic distribution law was followed in all cases of the coprecipitation of rare earth elements. Of the several variables studied which affected the logarithmic distribution coefficient, the most important were the pH value and the concentration of an organic acid. The coefficient decreased as the acid anion content increased. This can be attributed to the fact that the acid anion formed complex compounds with lanthanide and calcium. The distribution coefficients of several rare earth elements in producing the precipitate from a similar solution were closely related to their basicity or to the solubility of their oxalate salts. The order of the magnitude of the distribution coefficient was as follows: Lu>Y>Eu>Ce; this was in the reverse order of the basicity of rare earth elements or of the solubility of their oxalate salts.

The Coprecipitation Behavior of Strontium with Calcium Oxalate by Precipitation from a Homogeneous System. Masakazu Matsui. *Bulletin of the Chemical*

Society of Japan **39**, 581 (1966).—The coprecipitation of strontium with calcium oxalate was studied using dimethyloxalate to precipitate calcium from a homogeneous solution. The several effects of the coprecipitation conditions on the distribution coefficients were investigated in the fractional precipitation process of calcium-strontium oxalate mixtures. Regardless of the pH value, the concentration of acetic acid and other factors, the coprecipitation curves of strontium showed similar shapes in almost all cases, although, the curves well shifted up and down to some extent. It appears to be an anomalous system, because an increase in the fraction of the calcium precipitated tends to decrease the distribution coefficients. It is considered that two coprecipitation mechanisms are involved in the coprecipitation system; one is the surface adsorption on fine crystals, while the other is a normal systematic type. When the adsorption part was removed, it was found that the modified system obeyed the Doerner and Hoskins logarithmic distribution law and that the coefficient gave nearly a constant, 0.1.

The Solvent Extraction of Europium Ions with Benzoyltrifluoroacetone. The Synergistic Effect of Oxygen- and Nitrogen-containing Solvents. Tsunenobu Shigematsu, Masayuki Tabushi, Masakazu Matsui and Takaharu Honjyo. *Bulletin of the Chemical Society of Japan* **39**, 165 (1966).—The synergistic effect of many kinds of oxygen- and nitrogen-containing solvents on the extraction of europium ions with benzoyltrifluoroacetone in *n*-hexane has been studied. The addition of alcohols, esters, ketones, amines and heterocyclic compounds enhances the extraction, and in general, the solvents with longer carbon chain, especially alcohols and amines, have the larger synergistic effects. At a constant benzoyltrifluoroacetone concentration, the logarithm of the distribution coefficient is linear with pH. The slope of the log D vs. pH plot is about 1.5 in the extraction with 0.05 M benzoyltrifluoroacetone in *n*-hexane, but it is 2 in the presence of 0.04 M oxygen-containing compound and 3 in the presence of 0.04 M nitrogen-containing compound. It may be considered that europium benzoyltrifluoroacetonate forms some adducts with these oxygen- or nitrogen-containing Lewis bases, and that the coordination of nitrogen-containing Lewis bases to the chelates is stronger than that of oxygen-containing ones. Since the solvent extraction of neodymium and lutetium ions with β-diketones is performed as well as that of europium ions, it seems to be a favorable procedure for the extraction of rare earth ions with β-diketones to utilize the adduct formation between β-diketonates and active oxygen- or nitrogen-containing Lewis bases.

Fluorometric determination of yttrium with 5,7-dichlorooxine; Determination of yttrium in xenotime ore. Tsunenobu Shigematsu, Yasuharu Nishikawa and Keizo Hiraki. *Japan Analyst* **15**, 493 (1966), in Japanese.—Optimum conditions for the fluorometric determination of yttrium by 5,7-dichlorooxine was investigated and the method was developed to the direct determination of yttium in xenotime ore.

Some 250~500 mg portion of an ore sample was treated for 2~3 hours with 30~40 ml of hot concentrated H_2SO_4. The solution was diluted to 50~100 ml with water, and any insoluble residue was filtered. Sixty ml of 1 N oxalic acid was added to the solution and the pH was adjusted to 2.2. After standing for several

hours, the precipitate was ignited to obtain the total amount of rare earths oxide, from which was weighed out 25~50 mg. It was dissolved in HCl and diluted with water to adjust the concentration to 10 μg total rare earths oxide per ml. A 0.5~1.0 ml portion of the solution was transferred to a 100 ml beaker. To it were added 0.25 ml of 0.2 % 5,7-dichlorooxine, 20 ml of water and 5 ml of 20 % NH_4Cl solution. The yttrium-chelate was extracted with 25 ml of chloroform at pH 9.5, and the fluorescence intensity of the extract was measured.

Yttrium contents of xenotime and fergusonite samples were 20.29~29.81 % as Y_2O_3.

Inorganic Chemistry

Mössbauer Effect Study of V_2O_3. Teruya Shinjo and Koji Kosuge. *Journal of the Physical Society of Japan* **21**, 2622 (1966).—Mössbauer measurements on Fe^{57} doped in V_2O_3 were made in the temperature range from 4.2°K to 300°K. Above the metal-to-semiconductor transition temperature (~140°K), the absorption spectrum was perfectly paramagnetic. On the other hand, below the temperature, there appeared a magnetic hyperfine splitting (400 KOe at 4.2°K and 315 KOe at 131°K) and it was concluded to be due to an antiferromagnetic order of V_2O_3 in the low temperature phase. The internal field abruptly disappeared at the transition temperature associated with the first order transition. From the temperature dependence of the internal field, the fictitious Néel temperature of the low tempereratu phase was deduced to be in the vicinity of 200°K. The valence state of doped Fe seems to be trivalent in both phases.

Order-Disorder Transformation of Fe-Co Alloys in Fine Particles. Hajime Asano, Yoshichika Bando, Norihiko Nakanishi and Sukeji Kachi. *J. Japan Institute of Metals* **30**, 684 (1966), in Japanese.—Specific heat and lattice constant in b.c.c. of Fe-Co alloy were measured. The sample was obtained by reduction of $Fe_{1-x}Co_xC_2O_4 \cdot 2H_2O$ in H_2 at 800°C. The range of Fe-Co type order was between 30 and 75 at % Co. Transition of 550°C occurred between 21 and 50 at % Co, and in the range above 50 at % Co transition temperature decreased with increasing cobalt content. The lattice constant of Fe-Co alloy in the range of 40~60 at % Co increased by ordering, and that in the range of 23 ~ 40 at % decreased by ordering. Fe_3Co superstructure was not detected by neutron diffraction and Mössbauer effect.

Mössbauer Effect in Antiferromagnetic Fine Particles. Teruya Shinjo. *Journal of the Physical Society of Japan* **21**, 917 (1966).—Mössbauer measurements were made on the fine particles of an antiferromagnetic α-FeOOH with various particle sizes to examine the Mössbauer spectra in fluctuating fields produced by the relaxation of electron spins. In the ultra fine samples, the collapse of the internal field due to superparamagnetism was observed. The critical volume at 294°K was found to be $3\times10^{-17}cm^3$ and the critical temperature for the sample of $1\times10^{-17}cm^3$ to be 210°K. The effective anisotropy constant was estimated to be the order of 10^4 erg/cm^3. The transitional patterns from the ordinary magnetic splitting (6-line)

to the superparamagnetic doublet were discussed and the assignment of the doublet was attempted in comparison with Blume's prediction.

Antiferromagnetism of V_2O_3 Observed by the Mössbauer Effect. Teruya Shinjo, Koji Kosuge, Sukeji Kachi, Hideo Takaki, Masayuki Shiga and Yoji Nakamura. *Jorunal of the Physical Society of Japan* **21,** 193 (1966).—The Mössbauer effect of Fe^{57} doped in V_2O_3 was measured as a function of temperature. Ascertained are that the transition is from paramagnetic to antiferromagetic but the Néel temperature of the low temperature phase is much higher than the transition point.

The Magentic Property of β-Co(OH)$_2$. Toshio Takada, Yoshichika Bando, Masao Kiyama, Hiroki Miyamoto and Takashi Sato. *Journal of the Physical Society of Japan* **21,** 2726 (1966).—The magnetic property of $Co(OH)_2$ which has cadnium iodide type structure was experimentally studied by measurements of temperature dependence of magnetic susceptibility and magnetic field dependence of magnetization.

The samples were obtained by mixing $CoCl_2 \cdot 7H_2O$ aqueous solution with NaOH aqueous solution in the atmosphere of nitrogen gas.

β-Co $(OH)_2$ exhibited an atiferromagnetic behavior below 12.3°K. The susceptibility above 100°K also obeyed the Curie-Weiss law with a positive paramagnetic point (20°K). Effective Bohr magneton number was obtained to be $5.2\mu_B$. The magnetization gradually increased with increasing magnetic field until it was saturated by the field of about 35 KOe. From these phenomena the metamagnetic behaviors of β-Co $(OH)_2$ were made clear. In this case, it is suggested that the anisotropic field is smaller than the antiferromagnetic internal field and that the spin axis lies in c-plane.

The Magnetic Property of Ni(OH)$_2$. Toshio Takada, Yoshichika Bando, Masao, Kiyama, Hiroki Miyamoto and Takashi Sato. *Journal of the Physical Society of Japan* **21,** 2745 (1966).—The magnetic property of Ni $(OH)_2$ which has cadnium iodide type structure was experimentally studied by measurements of temperature dependence of magnetic susceptibility and magnetic field dependence of magnetization.

At the temperature below 30°K, $Ni(OH)_2$ was antiferromagnetic and the spin axis was directed in parallel to the c-axis. The susceptibility well above the Néel temperature obeyed the Curie-Weiss law with a positive paramagnetic Curie point (35°K). Effective Bohr magneton number was calculated to be $3.2\mu_B$. At 4.2°K, the magnetization $M_{/\!/}$, measured when the magnetic field was parallel to the c-axis of oriented $Ni(OH)_2$ powder, abruptly increased in the magnetic field about 55 KOe and was saturated by the field above 85 KOe. These phenomena allow to conclude that $Ni(OH)_2$ is metamagnetic; the magnetic moments within a metal ion layer form a ferromagnetic sheet and the moments in adjacent layers are antiparallel, such as in the case of $FeCl_2$.

***Mössbauer Effect of Fine Particles.** Teruya Shinjo. *Bussei* **7,** 589 (1966), in Japanese.—A brief review of the Mössbauer effect under the fluctuated magnetic fields is presented. Experimental results on fine particles are introduced and the superparamagnetism is discussed as a dynamic phenomenon of magnetic spin system.

It is suggested that the Mössbauer effect is a useful means to study the dynamic behaviors of magetic spins.

The cases of paramagnetic spin relaxation are included.

The Superstructure in Fine Aragonite Particles. Toshio Takada, Sukeji Kachi, Yuzuru Hiragi and Norihiko Nakanishi. *Bulletin of the Chemical Society of Japan* **23**, 2361 (1966).—An electron diffraction study was done with fine aragonite particles about 0.5 to 1.0 μ in size. The specimens were obtained by mixing a boiled calcium chloride solution (0.1N) with 0.1 N of an ammonium carbonate solution. Extra spots were observed with half-integer indices {1/2, 1/2, *l*}. This suggests the existence of a structure that differs from that of normal aragonite. From an X-ray diffraction study of the specimen, a {1/2, 3/2, *0*} diffraction was also observed. The structure for explaining these half-integer diffractions is presented as a superstructure of aragonite; it belongs to the space group of D_{2h}^{15}-Pbca, with cell dimensions of A=8.420 Å, B=9.385 Å, and C=5.741 Å, and it contains 8 formula units in a unit cell. A dark-image photograph shows this anomalous area to be comparatively wide and suggests that the anomalous area is dominant in a crystal. The authors conclude that rapidlyprecipitated aragonite powders contain a small quantity of the repeatedly-twinned crystals mentioned above.

Cation Distribution in Chemically Precipitated $ZnFe_2O_4$. Toshio Takada, Atsushi Hamamura, Masao Kiyama and Yoshichika Bando. *Japan Journal of Applied Physics.* **5**, 1246 (1966).—On the particles of $ZnFe_2O_4$ chemically precipitated from the aqueous solution, the relation between the preparation method and the cation distribution is investigated. The results are as follows:

(1) The fine particles of $ZnFe_2O_4$ rapidly co-precipitated from Fe^{3+}-Zn^{2+} mixed aqueous solution exhibited a superparamagnetic behavior. The superparamagnetism disappeared gradually by annealing above 300°C. From the result it is suggested that A-sites may be partially occupied by ferric ions in process of the formation of the crystal.

(2) The particles of $ZnFe_2O_4$ gradually precipitated from Fe^{2+}-Zn^{2+} mixed aqueous solution exhibited a paramagnetic behavior at room temperature, so that the cation distribution of the particles of $ZnFe_2O_4$ is equal to that of normal spinel ferrite.

The Crystallographic Study of Phase Transformation in Calcium Carbonate by Electron Diffraction. Toshio Takada, Yuzuru Hiragi, Sukeji Kachi and Norihiko Nakanishi. *Nippon Kagaku Zasshi* **87**, 1308 (1966), in Japanese.—Phase transformation from aragonite to calcite was studied by electron diffraction. Aragonite specimens were obtained by mixing a boiled calcium chloride solution with an ammonium carbonate solution. Calcite specimen was obtained by calcination of aragonite particles at 450°C for 30 min. The crystallographic relationships are follows:

$[\bar{1}10]_{Arg} /\!/ [\bar{1}2\bar{1}0]_{Calc}$

$(001)_{Arg} /\!/ (0001)_{Calc}$

From this relationship, the mechanism of transformation was discussed.

The Electron Spin Resonance Spectra of Nitrobiphenyl Radical Anions. Yasuto Nakai, Katsuyuki Kawamura, Kazuhiko Ishizu, Yasuo Deguchi, and Hideo Takaki. *Bulletin of the Chemical Society of Japan* **39**, 849, (1966).—A series of mono- and di-nitroliphenyl anion radicals has been studied by electron spin resonance when reduced electrolytically in N, N-dimethylformamide and by potassium in 1,2-dimethoxyethane. Hyperfine splitting constants for the nitrogen atoms have been estimated and discussed comparing with those of the nitrobenzene and calculating the spin density on the Hückel LCAO approximation.

Antiferromagnetism of V_2O_3 Observed by the Mössbauer Effect. Teruya Shinjo, Koji Kosuge, Sukeji Kachi, Hideo Takaki, Masayuki Shiga, and Yoji Nakamura. *Journal of the Physical Society of Japan* **21**, 193 (1966).—Temperature dependence of the internal magnetic field at Fe^{57} doped in V_2O_3 has been observed by the Mössbauer effect and it was found that the semiconductor V_2O_3 is antiferromagnetic at low temperature and transforms to be paramagnetic at the semiconducting-to-metallic transition temperature, and that from the sudden disappearance of the internal field at the transition temperature the Néel temperature of the semiconductor phase is not accord with but fairly higher than the transition temperature.

Localized Magnetic Moments in Mn_4N. Mamoru Mekata, Junsuke Haruna, and Hideo Takaki. *Journal of the Physical Society of Japan* **21**, 2267 (1966).—The temperature dependence of sublattice magnetizations and the specific heat due to magnetic ordering of Mn_4N were measured in order to study the origin of the anomalous thermomagnetic curve of the compound. The observed magnetization-temperature curves of two sublattices are more convex upwards than those of normal magnetic crystals. The discontinuity of specific heat at the Curie temperature was found to be 7.4 ± 1.0 cal/formula deg. which is much smaller than that expected on the assumption that the localized magnetic moments remain unchanged up to high temperatures. The average state density at the Fermi surface was estimated from the temperature independent magnetic susceptibility to be about 6/Mn eV. It was concluded from these facts that the high state density gives rise to large induced moments at low temperatures which depolarize with increasing temperature.

Studies on the Glazes of Lithia Cearmics Studies on the Thermal Shock Resisting Ceramics of the Li_2O-Al_2O_3-SiO_2 System, V. Toshio Maki and Megumi Tashiro. *Journal of the Ceramic Association of Japan* **74**, 89 (1966), in Japanese.—Glazes which are applicable to the lithia-ceramic bodies having extremely low thermal expansion coefficients [$\alpha < 20 \times 10^{-7}$/°C (room temperature~500°C)] were developed. The chemical composition of the glaze which showed the best result when applied to the lithiaceramic having the linear thermal expansion of about 5×10^{-7}/°C, is 50.4 SiO_2, 29.2 Al_2O_3, 5.9 Li_2O, 1.7 ZrO_2, 2.6 P_2O_5, 2.6 TiO_2, 1.0 Na_2O, 1.0 K_2O, 2.8 B_2O_3, 2.8 PbO wt. %.

The process of its application is as follows: A frit of the composition described above is added with 5 % clay powders and 0.05 % PVA and pulverized to a finess over 200 mesh by the wet process. The body to be applied with the glaze slip

is prepared by firing the pressed mixture of petalite and bentonite powders (100: 5 in wt. ratio) at 1260°C for one hour.

The body applied with the slip is dried and heated first at 1290°C in a furnace until the glaze melts and spreads over the surface of the body (for 5~10 min). It is then taken out from the furnace, put into another furnace previously set at 750°C, kept there for about 60 min. and then taken out from the furnace. By this second heat-treatment the glaze converts from glassy state to crystalline aggregates consisting almost of β-eucryptite crystallites, thus lowering its thermal expansion to fit that of the petalite body. The chemical durability of this glaze is satisfactory for use as dinner wares: No loss in gloss is observed for ist surface after immersed in the boiling 2 % citric acid solution. It also withstands quenching from 500°C into cold water without showing any cracking.

Crystallization of Glasses Containing BaO and TiO_2. Tadashi Kokubo, Sumio Sakka and Megumi Tashiro. *Journal of the Ceramic Association of Japan* **74**, 30 (1966), in Japanese.—In order to make barium titanate ceramics having high dielectric constant by a process of crystallization of glass, a series of glasses with the general composition $(100-x-y)\ BaO\cdot TiO_2+xSiO_2+yAl_2O_3$, in which x and y are within the range of 10 to 60 and 0 to 20 mole per cent respectively, was investigated, especially with respect to their glass formation tendencies, crystallization behaviors during reheating and dielectric properties of their crystallized products.

The glasses were melted, in all cases, in platinum crucibles at 1450°C for one hour and formed into plate of about 2 mm thick. They were crystallized by reheating up to 1100°C at a rate of 5°C/min.

The results of the experiments are summerized as follows:

1) A glass formation region was determined (cf. Fig. 1).
2) In general, crystallization of the glasses in this region starts at about 850°C, and is almost completed at 1100°C (cf. Fig. 3 and 5). The resulting crystallized products show flaws such as cracks and surface unevenness when the parent glasses contain $BaO\cdot TiO_2$ or Al_2O_3 in excess (cf. Fig. 2).
3) Major constituents of the crystallized products are $BaTiO_3$ (tetragonal), $BaAl_2Si_2O_8$ (hexagonal), $BaTiSiO_5$ and some unidentified crystalline phases (c.f. Table 2).
4) For the crystallized products with Al_2O_3 held constant, their dielectric constant decreases with increasing the $SiO_2/BaO\cdot TiO_2$ mole ratio. For those with $BaO\cdot TiO_2$ held constant, it reaches a maximum when the Al_2O_3/SiO_2 mole ratio is set to 35/65 (cf. Fig. 7). Generally, it increases with increasing the amount of barium titanate crystals separated out in the crystallized products. The composition of the crystallized product which shows a maximum dielectric constant (about 500 at 10^6c) in the present experiments is $BaO\cdot TiO_2$ 60, SiO_2 26, Al_2O_3 14 mole per cent.
5) On the basis of Bruggeman's theory the crystallized products obtained were assumed to have the structure of prophyritic mixture in which lamellar barium titanate crystals are dispersed in matrix consisting of glass phase and crystal phases of $BaAl_2Si_2O_8$ and $BaTiSiO_5$ etc. (cf Fig. 8).

Chemical Compositions of Glass-Ceramics. Megumi Tashiro. *Glass Industry* 47, 366 (1966),—The galass-ceramics developed heretofore can be classified into the following four types: Type A, Li_2O-containing glass-ceramics with high strength or low expansion coefficient (Li_2O-SiO_2, high Li_2O-low Al_2O_3-SiO_2, Li_2O-MgO or ZnO-Al_2O_3-SiO_2), Type B, Na_2O-containing glass ceramics of low cost (Na_2O-Al_2O_3-SiO_2), Type C, Nonalkaline glass-ceramics with low dielectric loss and high resistivity or of low melting (MgO or BaO-Al_2O_3-SiO_2, PbO or ZnO-B_2O_3-SiO_2) and Type D, glass-ceramics containing silica free crystal phases with high dielectric constants (BaO or PbO-TiO_2-Al_2O_3-SiO_2, PbO or Na_2O-Nb_2O_5-Al_2O_3-SiO_2).

The questions how their chemical compositions have been developed, how their compositions must be modified in order to improve qualities and to extend their applications to various industrial uses have been discussed.

Physical and Chemical Properties of Glass-Ceramics. Megumi Tashiro. *Glass Industry* 47, 428 (1966).—The results of the studies on the mechanical strength, the dielectric loss and the chemical durability of glass-ceramics carried out by the authors are summerized. Orowan's equation holds for the relation between the modulus of rupture of the glass-ceramics and the size of their constituent crystals. The dielectric loss of the glass-ceramics is primarily determined by the kind of their constituent crystals. Their chemical durability is strongly influenced by the properties of their glassy matrix.

Properties of Glass-Ceramics in Relation to their Microstructure. Megumi Tashiro. *Journal of Japanese Crystallographical Society* 8, (3) (1966).—The oxides having the cations with high electrostatic field such as Li_2O, MgO and ZnO are the necessray components in the base compositions of the glass-ceramics because of their active functions in promoting the two-phase separation of glass in the first stage of the process of heat-treatment. The ZrO_2, when introduced together with the P_2O_5 into their base compositions, accelerates the two-phase separation of glass, leading to the production of the glass-ceramics with low thermal expansion coefficients. The effects of the microstructure of the glass-ceramics on their modulus of rupture, dielectric loss and chemical durability are discussed.

Physical Chemistry

Electrocapillary Curves of Oil-Water Systems Containing Surface Active Agents. Akira Watanabe, Mutsuo Matsumoto and Rempei Gotoh. *Nippon Kagaku Zasshi* 87, 941 (1966), in Japanese.—The interfacial tension of oil-water interfaces changes with an applied potential. This phenomenon takes place over a reasonable polarization range, *i.e.* between ca. 20 and −20V, when the system has a sufficiently high electric conductance and contains surface active agents. The conditions were fulfilled in the present experiments by adding potassium chloride and ionic surface active agents to the water and oil phases, respectively. It was found that the interfacial tension decreased in the anodic or cathodic polarization range, depending upon whether the surface active agent was anionic or cationic. Here the sign of polarization was taken as that of the water phase with reference to

the oil phase. It was then concluded by the use of the Lippman-Helmholtz equation that the water side of the interface is charged positively or negatively for the respective case mentioned above. It appears that this charge is due to the counter ion layer corresponding to the adsorption of the ionic surface active agent at the oil side.

The formation of underwater films reconstituted with lecithin and their physico-chemical properties. T. Hanai. *Hyōmen* 4, No.10, 643 (1966), in Japanese. —In recent years, much attention has been paid by biologists as well as physical chemists to the study of underwater films composed of phospholipids to find a clue to the structure and the mechanism of biological cell membranes. The present treatise outlines some recent results of a series of physico-chemical approaches to the underwater films reconstituted with lecithin, and includes some descriptions on the formation of the films, the measurement of their electrical capacitance and resistance, and the comparison of the artificial films with biological cell membranes with regard to the thickness, the capacitance, the resistance, the surface tension, the permeability to water, and the breakdown voltage.

Crystallization of Amorphous of Titanium Dioxide Films Prepared by Vacuum-Evaporation. M. Shiojiri. *Journal of the Physical Society of Japan* 21, 335 (1966).— An electron microscopy and electron diffraction study was made on the structure of vacuum-deposited films of titanium dioxide. The films were amorphous when they were deposited on rocksalt at room temperature. When irradiated by an intense electron beam, the amorphous films crystallized in anatase and rutile forms. The rutile crystallities were small granules, whereas the anatase crystals grew to occupy larger areas of several microns in linear dimension. The difference in structure of the crystallized films seemed to be originated in the intrinsic properties of the amorphous films. The generation of dislocations which constituted small angle grain boundaries was observed in growing anatase crystals. In these crystals, twins were formed on the {112} planes and sidlocations were also observed in the individual grains.

Effect of Surface Characteristic of Particle on the Adhesion Property of Powders. M. Arakawa, T. Okada and E. Suito. *Journal of the Society of Materials Science Japan* 15, 151 (1966).—The adhesive property of powder is known to be very variable and also to be affected by the surface condition of the particle. In this experiment, the relation between the surface states of particles and the adhesive property of powders has been studied. The white alundum, calcium carbonate and kaolin clay were used as sample powders. The surface condition of white alundum and calcium carbonate were varied by adsorption of capric acid or sodium stearate, and kaolin clay were heat-treated. The adhesive property has been measured by final packing density ρ_f and coefficient K_1 in Kuno's equation at the first stage of packing or constant b in Kawakita's equation by the same tapping compress method. The attraction force between the particles at the contact point was measured by shearing test of powder bed. The results obtained are summarized as follows:

The effect of surface adsorbed layer of capric acid on white alundum is very

small compared with the influence of the particle size. But the treatment of calcium carbonate by sodium stearate is effective, and especially the packing density is affected largely, at humid atmosphere. The effect of this distinction of surface treatment upon both the powders is presumed to be the difference of mechanism of surface adsorption.

The adhesive property of kaolin clay when heat-treated, has changed remarkably at the fall of temperature of the crystal structure. The observed variation of the adhesive property has been compared with the reduction of the surface active site.

The adhesive force at the contact point between particles is not influenced by the surface adsorption layer on the white alundum.

Effect of Preparation of Solid Supports for Gas Chromatograhy on it's Specific Surface Area. E. Suito, M. Arakawa, M. Sakata and Y. Natsuhara. *J. Soc. Materials Sci. Journal of the Society of Materials Science Japan* **15**, 178 (1966).—Studies have been made of the adsorption of some organic vapours on various powders and solid supports for gas chromatography by the elution method with Shimadzu Sorptograph Model ADS-IA, and also bout nitrogen by the continuous flow method, which required a slight modification of the flow line in the instrument. The results give a typical BET type adsorption.

It was observed that the surface areas of the solid supports for gas chromatography decreased 1/5 1/10 through calcination with some flux, and that many of the micro pores were covered by HMDS (Hexamethyldisilazane)- silanization; this led to a presumption that big molecules such as acetone, are adsorbed only to its outer surface.

Differential Thermal Analysis of Complexes of Octadecylammonium with Steramide in Bentonite. E. Suito, M. Arakawa and T. Yoshida. *Kogyo Kagaku Zasshi* **69**, 1125 (1966).—The adsorption state of octadecylammonium ions (ODA) and steramide molecules (SA) between the lattice layers of bentonite lamellae has been studied by differential thermal analysis and X-ray diffraction. The DTA measurements were run in He or N_2 atmosphere.

The DTA curve of the (ODA+SA)-bentonite complex in which the ratio of ODA to SA was 1:1 showed a single endothermic peak at 360°C due to dissociation of organic compound of bentonite lamellae. In the case of the organic bentonite in which SA was in excess of ODA in amount two endothermic peaks due to the dissociation appeared at 330°C and 360°C. Conversely, the organic bentonite in which ODA was in excess of SA in amount gave two endothermic peaks near 360°C and 420°C, while the DTA curve of ODA-bentonite and SA-bentonite showed an endothermic peak due to the dissociation at 420°C and 330°C, respectively.

From the interpretation of each peak area of the DTA curves, it was concluded that the SA and ODA between the lattice layers of bentonite was associated in the mole ratio of 1:1.

Effect of Cleavage Steps of Muscovite on the Epitaxial Growth of Copper Phthalocyanine. E. Suito, N. Uyeda, M. Ashida and K. Yamamoto. *Proceedings of the Japan Academy* **42**, 54 (1966).—An optical and electron microscopic study was

attempted to find the relationship between the axial orientation of the vacuum deposited thin films of copper phthalocyanine and the cleavage step boundary of the substrated mica.

The results were interpreted in terms if stacking vector of mica subcell and its change at the step edge.

Electron Microscopic Observation on Heat Oxidation of Vacuum Deposited Aluminium Films. E. Suito, M. Shiojiri and H. Morikawa. *Japanese Journal of Applied Physics* 5, (1966).—It was found by electron microscopy that three kinds of oxides were formed on aluminium films by heat oxidation in air in addition to amorphous oxide forming a protective layer. They were morphologically different from one another, that is, (A) flower-like amorphous oxide, (B) plates of a single crystal of γ-Al_2O_3, and (C) dendrite crystals of γ-Al_2O_3. At 400°C type A, At 500°C type A and type B, and at 600°C type C as well as type B were formed. They all appeared preferentially at grain boundaries of metal aluminium. It is supposed that surface irregularities of the played an important role in the formation of these oxides.

The Polymorphism of Copper-Oxinate Crystal. E. Suito, M. Arakawa and T. Kobayashi. *Kolloid-Zeitschrift* (1966).—The transformation of copper-oxinate dihydrated was studied by electron microscopy and electron diffraction method. The replica method was also applied. The mechanism by which the unstable α-form is transformed into the stable β-form is as follows.

The deposition of unstable needle-like α-form crystal internal transformation of the α-form and the formation of intermediate fine particles, (γ-form) inter- and intra-particle condensation aggregation of the γ-form formation of the plate like β-form crystal by internal transformation of the aggregated and by the cementation of dissolved part.

The Phase Transformation of Copper-Oxinate Crystals Observed by Electron Microscopy. E. Suito, M. Arakawa and T. Kobayashi. *Kolloid-Zeitschrift & Zeitschrift für Polymere* **213**, No. 1-2, 135 (1966). — The transformation of copper-oxinate dihydrates was studied by electron microscopy and electron diffraction method. The replica method was also applied. The mechanism by which the unstable α-form is transformed into the stable β-form is as follows.

The deposition of unstable needle-like α-form crystal → internal transformation of the α-form and the formation of intermediate fine particles, (γ-form) → inter- and intra-particle condensation aggregation of the γ-form → formation of the plate like β-form crystal by internal transformation of the aggregates and by the cementation of dissoloved part.

Instrumental Features of 500 kV Electron Microscopes. S. Shimadzu, M. Iwanaga, K. Kobayashi, E. Suito, T. Taoka and H. Fujita. *Sixth International Congress for Electron Microscopy, Kyoto* (1966) 101-102 (Abstract)

The Effect of Electron Irradiation on the Thermal Transformation of Copper-Phthalocyanine. M. Ashida, N. Uyeda and E. Suito. *Sixth International Congress for Electron Microscopy, Kyoto* (1966) 447-448 (Abstract)

Observations on the Crytallization Process of Amorphous Thin Films. M. Shiojiri, H. Morikawa and E. Suito. *Sixth International Congress for Electron Microscopy, Kyoto* (1966) 467-468 (Abstract)

The Effect of Molecular Interaction on the Epitaxial Nucleation of Organic Crystals. N. Uyeda, M. Ashida and E. Suito. *Sixth International Congress for Electron Microscopy, Kyoto* (1966) 485 (Abstract)

Electron Diffraction Studies at Intermediate Energies (50 kV) in an Ultra High Vacuum Camera: Kinetics of the Oxidation of Copper Deposits. B.M. Siegel, N. Uyeda, J. Shin and J. Menadue. *Sixth International Congress for Electron Microscopy, Kyoto* (1966) 537 (Abstract)

Electron Microscopy and Crystal Chemistry. E. Suito and M. Shiojiri. *Kagaku (Kyoto)*, **21**, 35 (1966).

Effect of Particle Surface on the Cohesion and Adhesion Phenomena of Powders. M. Arakawa. *Journal of Research Association of Powder Technology, Japan.* 14 (1966).

Surface Structures of Powder Particles. E. Suito. *Journal of the Society of Materials Science Japan*, **15**, 120 (1966).

Polymer Chemistry

Normal Stress Effect in Dilute Polymer Solutions. I. Polystyrene in Dioctyl Phthalate. Mikio Tamura, Michio Kurata, Kunihiro Osaki, and Katsuhisa Tanaka. *Journal of Physical Chemistry* **70**, 516 (1966).—Normal stresses of a series of polystyrene solutions in dioctyl phthalate (poor solvent) were measured with a parallel-plate rheogoniometer in the range of concentration, 0.8~2.0 wt %. The shear stress and dynamic moduli were also measured in the same range of concentration with a coaxial cylinder rheometer. It was found that the incremental normal stress attributable to the polymer was primarily exerted in the flow direction and that $\sigma_{11}-\sigma_{33}$ was proportional to κ^2 and c/M over a wide range of variables. Here σ_{11} is the normal stress in the flow direction, σ_{33}, is the normal stress in the direction perpendicular both to the flow line and the sheared plane, κ is the rate of shear, c is the polymer concentration in grams per cubic centimeter, and M is the molecular weight.

Normal Stress Effect in Dilute Polymer Solutions. II. Polystyrene in Chlorinated Diphenyl. Kunihiro Osaki, Katsuhisa Tanaka, Michio Kurata, and Mikio Tamura. *Journal of Physical Chemistry* **70**, 2271 (1966).—Normal stresses of a series of 0.3-2.0 wt.% polystyrene solutions in chlorinated diphenyl (good solvent) were measured with a parallel plate rheogoniometer. The shear stresses and the complex moduli were also measured with a coaxial cylinder rheometer. The normal stress $(-\partial P/\partial \ln r)$ and shear stress $(\sigma_{12}-\kappa\eta_s)$ were linear in κ^2 and κ, respectively, in the lowest range of shear rate κ observed. The ratios $(-\partial P/\partial \ln r)/\kappa^2$ and $(\sigma_{12}-\kappa\eta_s)/\kappa$

decreased with increasing rate of shear more rapidly than did those of polystyrene solutions in dioctyl phthalate (poor solvent). It was also found that both the normal stress and shear stress were proportional to the number of polymer molecules per unit volume, n. For a wide variety of molecular weights and concentrations, the reduced (or intrinsic) normal and shear stresses, $(-\partial P/\partial \ln r)/n$ and $(\sigma_{12}-\kappa\eta_s)/n$, were found to be universal functions of the reduced rate of shear $(\eta_0-\eta_s)\kappa/n$. The effect of heterogeneity in molecular weight was also investigated through a comparison of the data obtained for ordinary fractionated samples and an anionically polymerized sample.

Hydrodynamic Properties of Flexible-Ring Macromolecules. Masaaki Fukatsu and Michio Kurata. *Journal of Chemical Physics* **44**, 4539 (1966).—The sedimentation constant of a series of multiple-ring macromolecules has been calculated by the method of Kirkwood. The multiple-ring form consists of m subrings of equal size linearly connected by universal joints. In the limit of large intersegmental hydrodynamic interaction, the ratio of the sedimentation constant of a multiple-ring molecule to that of a linear chain of the same molecular weight is 1.18 for $m=1$, 1.32 for $m=2$, 1.40 for $m=3, \cdots$ and 2.00 for extremely large m. These values are found to be practically independent of the excluded volume effect.

The intrinsic viscosity of a single-ring macromolecule has also been calculated by the method of Zimm. The eigenvalue problem encountered in the Zimm theory can be solved exactly over the whole range of the hydrodynamic interaction parameter, $h=0$ to ∞. The ratio of intrinsic viscosities of ring and linear molecules is 0.500 for $h=0$ (free-draining case) and 0.645 for $h=\infty$ (non free-draining case). The latter value is slightly modified if the hydrodynamic interaction is treated by the Fixman method.

The Θ Condition for Random and Block Copolymers of Styrene and Methyl Methacrylate. Tadao, Kotaka, Hiroshi Ohnuma and Yoji Murakami. *Journal of Physical Chemistry* **70**, xxxx (1966).—For random and block copolymers of styrene and methyl methacrylate, the θ temperatures are determined in cyclohexanol and 2-ethoxtethanol. The former has nearly equal Θ temperatures for both of the parent homopolymers, polystyrene and poly (methyl methacrylate). While the latter is a nonsolvent toward polystyrene but a poor solvent toward poly(methyl methacrylate). Quite significant difference is found between the Θ temperatures of the random and the block copolymers. At the θ conditions, the intrinsic viscosity of the random copolymers is proportional to the square root of molecular weight $M^{1/2}$. On the other hand, the viscometric behavior of the block copolymers are quite different in the two solvents.

Homogeneous Hydrolysis of Esters with Polymer Sulfonic Acids. Ichiro Sakurada, Yasuyoshi Sakaguchi, Tomoyoshi Ono, and Toshio Ueda. *Die Makromolekulare Chemie* **91**, 243 (1966).—Studies on homogeneous hydrolysis were carried out of low molecular esters with polymeric sulfonic acids such as polyvinylsulfonic acid, copolymers of vinyl sulfonic acid and styrene, sulfonated polystyrenes, *etc.*

In an aqueous solution of polymeric sulfonic acid, hydrogen ions, which contribute to the hydrolysis, are found only in the neighbourhood of polymer molecule,

and in dilute solution there is a region where no hydrogen ion being able to contribute to the hydrolysis exists; as a result, the hydrolysis takes place only in the neighbourhood of polymer molecule. When longer alkyl ester such as butyl acetate is hydrolysed with partially sulfonated polystyrenes, the ester molecules are bound by hydrophobic interaction between a benzene ring and the alkyl group to result in a higher concentration of ester in the neighbourhood of polymer molecule. In such a case, the rate of hydrolysis by a polymeric sulfonic acid is for example more than ten times greater than that of hydrolysis with hydrochloric acid. When no concentration of ester around polymer catalyst occurs, there is apparently no difference between the rates of hydrolysis by polymer catalyst and hydrochloric acid.

It was further shown that esters which contain an amino group are hydrolysed with polystyrenesulfonic acid with a much higher rate than with hydrochloric acid due to its electrostatic interaction with the polymeric sulfonic acid.

Radical Polymerization of 3-Chloromethyl-3-Allyloxymethyl-Oxetane. Ichiro Sakurada, Kaishi Noma, and Yoshio Ohfuji. *Chemistry of High Polymers* **23**, 172 (1966), in Japanese.—3-chloromethyl-3-allyloxymethyl-oxetane, a "two-stage-polymerizable" monomer, was synthesized and polymerized in bulk with benzoyl peroxide or α,α'-azobisisobutylonitrile. The degrees of polymerization of polymers obtained were extremely low. Even when a large amount of initiator was used, the limited conversion was very low. These facts suggest that degradative chain transfer to the monomer, which has often been observed in polymerizations of other allyl compounds, is predominant also in these polymerization systems. The ratios of the propagation or initiation rate constants to the degradative chain transfer to the monomer were calculated for the macroradicals (k_p/k_{tr}) and the primary radicals(k_i/k_{tr}'). The former was 6, and the latter 0.3. From the infrared spectra it was confirmed that the oxetane rings in the polymer molecules could be easily opened by treating the polymer with boron trifluoride etherate.

Experimental Determination of Elastic Moduli of the Crystalline Regions in Oriented Polymers. IX. Isotactic Polybutene-1 Ichiro Sakurada, Katsuhiko Nakamae, Keisuke Kaji and Susumu Wadano. *Chemistry of High Polymers* **23**, 696 (1966), in Japanese.—Elastic modulus of the crystal lattice parallel to the chain axis (E_l), for isotactic polybutene-1 (Isot. PB) was determind by an X-ray diffraction method. The modulus was found to be

Isot. PB: $E_l=25\times10^4$kg/cm^2 (25 ± 1°C).

Natte et al. reported that the chains of Isot. PB assumed the conformation of a three-fold helix in the crystalline state.

The above E_l-value for Isot. PB was discussed in terms of the force required to stretch a molecule by 1% and was compared with the E_l-values for isotactic polypropylene, isotactic polybutene-1 and isotactic polystyrene which also assumed the same conformation of the chain skeleton as Isot. PB in the crystalline state.

Experimental Determination of Elastic Moduli the Crystalline Regions in Oriented Polymers. VIII. Polytetrahydrofuran. Ichiro Sakurada, Katsuhiko Nak-

amae, Keisuke Kaji and Susumu Wadano. *Chemistry of High Polymers* **23**, 651 (1966), in Japanese.—Elastic modulus of the crystal lattice parallel to the chain axis (E_l), for polytetrahydrofuran (PTHF) was determined by an X-ray diffraction method. The modulus was found to be

PTHF: $E_l = 55 \times 10^4 \text{kg/cm}^2$ $(20 \pm 1°\text{C})$.

Imada et al. and Cesari et al. recently reported that the molecular chain of PTHF assumed a planar zig-zag conformation in the crystalline state and a small cross-sectional area of $17.1 \times 10^{-16} \text{cm}^2$. The force constants of bond-streching and of bond-bending for C-O and C-O-C are reported to be rather greater than those for C-C and C-C-C. This seems to make it difficult to understand the result for PTHF which showed much lower value of E_l compared with that for polyethylene ($E_l = 240 \times 10^4 \text{kg/cm}^2$). One of explanations for this may be that the chain of PTHF does not assume fully extended structure in the crystalline state.

Ionic Polymerization under Electric Field. II. Radiation-Induced Polymerization of Styrene. Ichiro Sakurada, Norio Ise, and Seiji Kawabata. *Die Makromolekulare Chemie* **97**, 17 (1966).—Radiation-induced polymerization of styrene was carried out at −78°C. in methylene chloride under strong electric field. The rate of polymerization was enhanced in the presence of electric field whereas the degree of polymerization remained virtually unaffected. It was pointed out that the enhancement of the rate could be accounted for by the increase of ion yield due to the field, assuming free ion mechanism. The electric conductivity of the polymerizing solution was suggested to be mainly due to an electrolyte produced by solvent radiolysis. Using ethylbenzene and toluene instead of methylene chloride, which are believed to be fairly stable to the radiation, the conductivity was measured. From the measurements, the average life time of ions supposedly from styrene molecule was estimated to be $10^{-1} \sim 10^{-2}$ sec., which are believed to be responsible for the radiation-induced polymerization.

Hydrolysis of Polymeric Esters with Polymeric Sulfonic Acids. III. Hydrolysis of Partially Acetylated Products Modified Polyvinyl Alcohols and Starchs with Polymeric Sulfonic Acids. Ichiro Sakurada, Yasuhiro Ohmura and Yasuyoshi Sakaguchi. *Chemistry of High Polymers* **23**, 735 (1966), in Japanese.—Partially acetylated products of branched polyvinyl alcohols (PVA) (branched units <1.3/100 unit molecules), vinyl alcohol-allyl alcohol copolymers (mol% of allyl alcohol <22) and vinyl alcohol-isopropenyl alcohol copolymers (mol % of isopropenyl alcohol<18) were hydrolyzed with polystyrene sulfonic acid, partially sulfonated polystyrene and dodecylbenezene sulfonic acid in water, and the rate constants of hydrolysis (k_s) were compared to those of hydrolysis carried out under the same condition with hydrochloric acid (k_{HCl}). Generally the values of $r = k_s/k_{HCl}$ for acetates of these modified PVA were near those for acetates of linear unmodified PVA. Partially acetylated starchs were also hydrolyzed, and it was found that the r-values were much smaller than those for partially acetylated PVA of the same acetylation degree. The r-value for partially acetylated amylose was somewhat greater than that for partially acetylated amylopectin. Some discussions were given for these results.

Ionic Polymerization under Electric Field I. Cationic Polymerization of p-Methoxystyrene. Ichiro Sakurada, Norio Ise, and Takao Ashida. *Die Makromolekulare Chemie* **95**, 1 (1966).—The cationic polymerizations of *p*-methoxystyrene with iodine in ethylene dichloride were carried out under strong electric field. It was found that the overall rate of polymerization was larger in the presence of the electric field than in its absence. After confirming that the field effect is neither due to the JOULE heat, nor related to the polymerization initiation by ionic species or radical electrolytically produced, it was suggested that the field-facilitated dissociation of ion-pairs at growing chain ends may be responsible for the observed field effect, on the assumption that the rate constant of propagation of free ions was larger than that of ion-pairs.

It was also noticed that the degree of polymerization became larger under electric field.

The radical polymerizations of styrene and methylmethacrylate were also performed under electric field. No field effect was observed in contrast to the cationic polymerization.

Radical Copolymerizations of 3-Chloromethyl-3-Allyloxymethyl-Oxetane with Some Vinyl Monomers. Ichiro Sakurada, Kaishi Noma and Yoshio Ohfuji. *Chemistry of High Polymers* **23**, 234 (1966), in Japanese.—Radical copolymerizations of 3-chloromethyl-3-allyloxymethyl-oxetane (CAO) with vinyl acetate (VAc), styrene (St) and maleic anhydride (MAH) were carried out. The behaviors of the polymerizations and some properties of the copolymers obtained were investigated. CAO and VAc could be easily copolymerized and copolymers of various composition were obtained. The monomer reactivity ratios at 65°C were $r_{CAO}=0.22\pm 0.01$ and $r_{VAc}=1.36\pm 0.01$. For CAO-St systems, it was difficult to obtain copolymers having large CAO contents. From these results the *Q-e* value of CAO was calculated as follows: $R=0.030$ and $e=-1.40$. Copolymerization of CAO and MAH proceeded very smoothly. From the results of the analyses of copolymers, it was suggested that CAO-MAH copolymer had an alternate structure. All copolymers obtained were soluble in various organic solvents, but, by treating with boron trifluoride etherate, CAO-VAc and CAO-MAH copolymers became insoluble.

Experimental Determination of Elastic Moduli of the Crystalline Regions in Oriented Polymers. VI. Isotactic Polyvinyl *tert*-butyl ether. Ichiro Sakurada, Katsuhiko Nakamae, Keisuke Kaji and Susumu Wadano. *Chemistry of High Polymers* **23**, 335 (1966), in Japanese.—Crystal deformation of isotactic polyvinyl *tert*-butyl ether (PV*t*BE) was studied. The chain of PV*t*BE assumes in the lattice the conformation of a four-fold helix. It was shown that PV*t*BE has a tetragonal unit cell, regardless of the stress applied in the present study. The elastic modulus (E_l) of the crystalline region in the direction of the chain axis was calculated to be 4.1×10^4 kg/cm^2 (25 ± 1°C). This value is the smallest among those found for several crystalline polymers. The above elastic modulus was discussed in terms of the chain skeleton conformation in the crystal, together with the results obtained by us for the extensibilities of helical polymers.

Studies on the Molecular Structure and Physical Properties of Crystalline Polystyrene. I. Crystallinity of Isotactic Polystyrene. Waichiro Tsuji, Ryozo Kita-

maru and Fumio Sakaguchi. *Chemistry of High Polymers* **23**, 836 (1966), in Japanese.-Polymerizations of styrene were carried out by various catalytic systems in order to investigate the correlation between the stereoregularity and the crystallinity. The maximum degree of the crystallinity was estimated by X-ray spectrum, density measurement and differential thermal analysis methods. It was found that the solubility in hot acetone as a measure of stereoregularity for each product had an intimate relation to the maximum degree of crystallinity of the fraction of the product insoluble in hot acetone.

From the study of the infrared spectra in solution state, the absorption bands at $1076cm^{-1}$ and $583cm^{-1}$ were used to estimate quantitavely the relation between the stereoregularity and crystallinity. It was found that there was linear relationship between the maximum degree of crystallinity and these two absorption bands, being characteristic polystyrene. In addition, it was confirmed by studying the infrared spectra of copolymers of styrene and propylene, that the absorption band at $583cm^{-1}$ may be used to characterize the stereoregularity of polystyrene.

Chemical Treatment of Cotton by the Graft Copolymerization of Reactive Monomer, and Cross-Linking. II. Glycidyl Methacrylate. Waichiro Tsuji, Tetsuo Ikeda and Yoriko Kadono. *Sen-i Gakkaishi* **22**, 504 (1966), in Japanese.—Glycidyl methacrylate was graft polymerized onto cotton by simultaneous Co^{60} γ-ray irradiation in the presence of air at room temperature. During the graft polymerization, epoxy rings in the grafted side chains did not open by the irradiation of the total dose below 2×10^5r, but insoluble homopolymer was formed above this dose.

As the grafted cotton has reactive epoxy rings in the grafted side chains, long chain crosslinkings can be introduced to the cotton cellulose using these reactive groups.

The crease recovery and some tensile properties of the grafted and cross-linked cottons were examined.

The results may be summarized as follows:

(1) Dry crease recovery of the grafted cottons cured after treated with H_3PO_4-methyl ethyl ketone, HCOOH-morpholine and ethylene and ethylene glycol-BF_3 respectively increases considerably, but no improvement is observed in wet crease recovery.

(2) Curing of the grafted cottons treated with of with ethylene diamine or bis (hydroxy ethyl) sulfone gives no effects on improving both the dry wet crease recoveries.

(3) Curing of the grafted cottons treated with $Zn(BF_4)_2$ solution gives a considerable impovement in both the dry and wet crease recoveries.

(4) Though the strength of warp of the grafted cotton fabric is decreased by cross-linking, the tensile damage of cotton by cross-linking is remarkably prevented by the grafting.

The Unperturbed Dimensions of Polypropylene and Polyethylene. Hiroshi Inagaki, Takeaki Miyamoto and Shigeyasu Ohta. *The Journal of Physical Chemistry* **70**, 3420 (1966).—The unperturbed dimensions for propylene polymers with differ-

ent stereospecificities are compared with those for polyethylene. Two types of syndiotactic polypropylene have been prepared at −78° with the catalytic system VCl_4-anisol-$Al(C_2H_5)_2Cl$ by using toluene and *n*-heptane as solvents for polymerization, respectively. Tacticities of these polymers range from 0.8 to 1.5 as determined by the relative absorption intenisty at 867cm^{-1} (infrared index). Determination of molecular weights, M, of six fractions having an infrared index of *ca.* 0.8 was made in heptane by the Archibald ultracentrifugal method and by light scattering. Intrinsic viscosities $[\eta]$ of these fractions were determined in different solvents. Isoamyl acetate is found to be a θ solvent for the syndiotactic polymer and the θ temperature is elevated from 34° to over 70° with an increase in the infrared index from 0 to 1.5. Relationships between $[\eta]$ and M obtained by various authors for polypropylene fractions, including our own data for the syndiotactic polymer, are analyzed using our recent semiempirical equation and the Stockmayer-Fixman equation for estimating the unperturbed dimensions. The unperturbed dimensions of propylene polymers are greatly influenced by temperature, showing a negative temperature coefficient, but are only slightly influenced by the choice of solvent. The characteristic ratios $\langle R^2\rangle_0/nl^2$ evaluated with the proper data at 135° in decalin, assuming that the Flory constant Φ_0 is 2.87×10^{-22} cgs, averge about 5.0, 4.3, and 4.7 for atactic, isotactic, and syndiotactic polypropylene, respectively. These ratios evaluated with the proper data at room temperature in different solvents converge around 5.9 and 6.1 for the atactic and syndiotactic polymer, respectively. The latter ratios are explicable in terms of a theoretical prediction recently made by Flory, Mark, and Abe. According to these results, it is concluded that the characteristic ratio obtained at 135° in decalin for polyethylene, 6.1, is significantly higher than those for polypropylene with any stereospecificity. In connection with this conclusion, a qualitative discussion is made on the correspondence of molecular conformations assumed in the solid state to those in solution.

Einkristalle von syndiotaktischem Polypropylen aus verdünnter Lösung. H. Inagaki und T. Miyamoto. *Die Makromolekulare Chemie.* **97**, 267 (1966)— in German. The fact that the stereoregular chain polymers in solid assume proper conformations relevant to each but behave as random coils in solution has been well confirmed. The purpose of the present paper is to study whether a chain conformation assumed in solid be retained still in solution. Basing on our previous result of the unperturbed dimensions of propylene polymers with different stereospecificities (J. Phys. Chem. **70**, (1966) 3420), a hypothesis for the retention of chain conformation in solution has been proposed. An indirect evidence for this hypothesis is presented here by investigating dilute solution grown single crstals of syndiotactic polypropylene. Further, a discussion for the mechanism of single crystal growth followed by the primary nucleus formation is given in due course.

Shear-Rate Dependence of the Intrinsic Viscosity of Flexible Linear Macromolecules. Tadao Kotaka, Hidematsu Suzuki and Hiroshi Inagaki. *The Journal of Chemical Physics* **45**, No. 8, 2770 (1966).—Shear-rate dependence of the intrinsic viscosity has been studied on polystyrene in four different solvents by using a

Zimm-Carothers rotational viscometer and Ubbelohde viscometers. The former viscometer was employed particularly for measuring zero-shear intrinsic viscosity $[\eta]_0$. The results are summarized in terms of the $[\eta]/[\eta]_0$ versus generalized rate of shear $\beta=([\eta]_0\eta_s M/RT)G$, where η_s is the solvent viscosity, M the solute molecular weight, G the rate of shear, and others have usual significance. It has been found that, (i) at the values β below 0.1, $[\eta]$ is practically independent of rate of shear (or shear stress); (ii) the non-Newtonian effect does exist even in θ conditions; and (iii) at the values of β below 2, the $[\eta]/[\eta]_0$-vs-β curves of the systems with different molecular weights and in different solvents give a single composite curve, which fairly well resembles to the curve of a prolate ellipsoid with the axial ratio $p=3$.

A Semi-Empirical Method for Estimating Unperturbed Dimensions of Chain Polymers from the Intrinsic Viscosity-Molecular Weight Relationship. Hiroshi Inagaki, Hidematsu Suzuki and Michio Kurata. *Journal of Polymer Science* Part C No. 15, 409 (1966).—A semi-empirical method for estimating unperturbed chain dimensions from relationships between intrinsic viscosity $[\eta]$ and molecular weight M is proposed. This method is based on combining the Ptitsyn equation of the excluded volume effect with a semiempirical relation between two expansion factors α_η and α for the hydrodynamic radius and the end-to-end distance, respectively, i.e., $\alpha_\eta^3=\alpha^{5/2}$, which has been suggested by Yamakawa and Kurata. This combination gives $([\eta]/M^{1/2})^{4/5}=0.786K^{4/5}+0.950\text{-}K^{4/5}z^{*2/3}M^{1/3}$ for large α, presumably for than 1.4. Experimental tests are made with viscosity data obtained for polystyrene fractions in *trans*-decalin, benzene, and butanone and also with those obtained for poly (methyl methacrylate) in various solvents. Light-scattering data by Berry are discussed in the light of present results. The parameter B describing long-range interactions is found to be nonlinearly related to the reciprocal of temperature $1/T$, that is, the quantity B_0 as defined $B/[(1-(\theta)/T)]$ is a decreasing function of T. On the basis of experimental result, disagreement between two B values deduced from *intra*-and *inter*-chain interactions is pointed out.

Studies on the Nonwoven Fabric (II) Properties of Nonwoven Fabrics Using Various Binders. Waichiro Tsuji, Masazo Imai, Koichi Sugita, Yoichi Kanayama, and Toshio Hirata. *Journal of the Adhesion Society of Japan* 2, 8 (1966), in Japanese.—Dry process non-woven fabrics based on the webs of Tetoron, rayon, Exlan and vinylon were prepared by our laboratory equipment using eight different binders, four of which were non-reactive type and the others reactive type.

The binder contents in the fabrics were 70-100% by weight of webs. No evident difference was given to the tensile and tear strength by the use of any kinds of binders, reactive or non-reactive type More flexible binder resin resulted in softer fabric. With reactive type binders better crease recovery was given than with non-reactive type binders.

Good crease recovery given by the use of polyvinylidene chloride-type binder is considered as the result of insufficient adhesion of the resin to the web fiber. Solvent resistance is attributed to the cross-linking effect of the binder, and was

shown to be indifferent to the kind of the web fiber.

The non-woven fabrics prepared by using reactive type acrilic or NBR binders seem to be most suitable for padding, judging from the properties of fabrics shown in this study.

Moleceular Structure and Some Related Properties of polyethylene Stretched in the Amorphous and Crystalline States. Hyong-Dong Chu, Ryozo Kitamaru, and Waichiro Tsuji. *Annual Report of the Institute of Chemical Fiber, Kyoto University*, **23**, 1 (1966), in Japanese.—The molecular orientation of stretched polyethylene has been estimated separately for the crystalline and amorphous phases by using x-ray and birefringence techniques. It is confirmed that if a lightly crosslinked polyethylene is highly stretched rapidly in the perfectly molten state and cooled to room temperature, a fibrous structure comprised of highly oriented crystallites and almost unoriented relaxed amorphous chains is produced. Some properties such as dynamic mechanical properties and thermodynamic property are discussed in relation to the molecular structure.

Molecular Structure and Some Related Properties of Polyethylene Stretched in the Amorphous and Crystalline States. Hyong-Dong Chu, Ryozo Kitamaru, and Waichiro Tsuji. *Journal of Applied Polymer Science* **10**, 1377 (1966).—The molecular orientation of stretched polyethylene has been estimated separately for the crystalline and amorphous phases by using x-ray and birefringence techniques. It is confirmed that if a lightly crosslinked polyethylene is highly stretched rapidly in the perfectly molten state and cooled to room temperature, a fibrous structure comprised of highly oriented crystallites and almost unoriented relaxed amorphous chains is produced. Some properties such as dynamic mechanical properties and thermodynamic property are discussed in relation to the molecular structure.

Pyrolysis of Wool in Sealed Tubes. Masao Horio, Takashi Kondo, Ken'ichi Sekimoto and Makoto Funatsu. III[e] *Congrés Internationale de la Recherche Textile Lainière* **2**, 189 (1965), published in 1966.—Wool fibers were heated in various atmospheres in sealed tubes. The maximum temperature was varied from 60° to 250°C and the duration was changed from 1 to 6 hours. The change in color, microscopic structure and birefringence were observed. Furthermore, elementary analyses and amino acid determination were performed. The wool fibers are very stable against heating when they were thoroughly pre-dried and then heated in a dehydrated medium. Under this condition the fibers are only little damaged even at 250°C, while the ordinary air-dried fibers containing about 10% of moisture lose their scaly structure at 150°C and are fused into a dark melt at 200°C. The change in birefringence at pyrolysis in various media showed how sensitively it is influenced by the moisture content of atmosphere. The polarization microscopic observations revealed that the paracortex is more sensitive to heating than the ortho-cortex, and both cortices separate from each other when the air-dried fibers were heated at 150°C in a sealed tube. The amino acid analyses of both cortices showed that only the change in cystine content was very distinct, and it became almost zero when the air-dried fibers were heated at 150°C in a sealed tube. Notwithstanding, the sulphur content of wool were only reduced by half.

This suggests that the disulphide bonds would be splitted producing the cystein and cysteic acid, and the former decomposes by giving off the hydrogen sulphide. The gas evolved during pyrolysis was analyzed by gas chromatographic technique and a series of mercaptan besides hydrogen sulphide were indentified.

Histochemical Studies on Chemically Modified Wool. M. Horio, T. Kondo, Y. Nakamura, H. Sugiyama, K. Nishiumi and M. Tani. Reprints of Scientific Papers, X-14, 1-5-04, *International Symposium of Macromolecular Chemistry*, 1966.— Wool fibers were modified by methylation and dinitrophenylation, and the change in amphoteric behavior was observed. The acid absorption of wool is markedly decreased by methylation, because the ionization of carboxyl groups is depressed by esterification. In agreement with this the absorption of acid dyes increases, while that of basic dyes decreases by methylation. The acid character of wool is remarkably depressed by esterification, and the apparent isoelectric point of methylated wool determined by the histochemical method is about 8.0 against 5.6 of the original wool. The dinitro-phenylation brings about quite the opposite effect. Since the basic residues are blocked by 2,4-dinitrophenyl groups the wool becomes more acidic than the original wool and increases the accessibility to basic dyes, while decreases the accessibility to acid dyes. The apparent isoelectric point of dinitrophenylated wool was determined to 3.7.

Orientation of (101) Planes of Cellulose during Fiber and Sheet Formation from Viscose. Masao Horio, Keinosuke Kobayashi and Toshisada Takahashi. Reprints of Scientific Papers, VII-182, 4-5-15, *International Symposium of Macromolecular Chemistry*, 1966.—(1) In the course of sheet formation from viscose the (101) planes are oriented parallel to the film surface more distinctly in proportion to the contents of sulphates in the coagulation bath. Since hydroxyl groups exist concentrated on (101) planes, they are most hydrophilic and chemically reactive. The dehydration due to the osmosis whose effect depends upon the amounts of sulphates in coagulation bath causes water to flow perpendicular to the boundary surface, and this urges the (101) planes to be arranged parallel to the film surface. (2) Quite the similar effect takes place at the spinning of viscose filaments. (3) Because water molecules intervene mostly in the spaces between (101) planes, the dimension change of films and fibers having a higher order of planar orientation is different from that of unoriented materials. In general the change in surface area of highly oriented materials is very small. (4) The salts of cellulose xanthate of polyvalent metals of subgroup "b" and group VIII of peridical table are apparently amorphous, but the elimination of metallic elements leads to the highly oriented cellulose. Under the conditions at which the regeneration of cellulose takes place rapidly, the modification of Cellulose IV is produced. The mechanism was elucidated.

High-Voltage Electron Microscopy. G. F. Bahr, E. H. Zeiter and K. Kobayashi. *Journal of Applied Physics* 37, 2900 (1966).—An increase of the acceleration voltage in conventional transmission microscopy yields reduced damage to the specimen and a potentially higher resolving power, and permits an increase in specimen

thickness. These gains as a function of voltage are discussed and partly confirmed by experiments. The differential gains above 500 kV are very small, yet costly. A range up to 1000 kV for conventional high-voltage electron microscopy can be recommended.

Organic Chemistry

The Reaction of Oxymercurials with Active Methylene Compounds and the Demercuration of the Resulting Mercurials with Acid and Base. Katsuhiko Ichikawa, Osamu Itoh, Takahisa Kawamura, Mutsuzo Fujiwara, and Tamotsu Ueno. *Journal of Organic Chemistry* **31**, 447 (1966).—The reaction of oxymercurials with active methylene compounds has been studied in acetic acid, methanol, ethanol, and 2-propanol containing perchloric acid. Active methylene compounds, substituted with alkyls and aralkyls containing mercury, have been obtained in good yields. This reaction proceeds readily in between the oxymercurials from 1-olefins and the active methylene compounds whose keto-enol equilibria are on the side of the enol form. Oxymercurials from inner olefin and substituted olefin failed to react because of side reactions. 3,3-Diacylpropylmercuric chlorides, which were obtained by the reaction of β-diketones, reacted with aqueous potassium hydroxide to give 1,1-diacylcyclopropanes and mercury through an SNi mechanism. In methanol, ethanol, and 2-propanol containing perchloric acid, 3,3-diacetylpropylmercuric acetate gave 1,1-diacetylcyclopropane at lower reaction temperature. At higher temperature, mixtures of the cyclopropane and methyl or ethyl 3,3-diacetylpropyl ether were obtained. The demercuration of the same acetate in acetic acid containing perchloric acid gave pentan-1-ol-4-one acetate and 3-acetyl-2-methyl-4,5-dihydrofuran. For this acid demercuration, a mechanism involving a nonclassical carbonium ion intermediate, which is analogous to phenonium ion, can be described. This was disproved, however, by several experimental results. It is concluded that this reaction proceeds through a classical carbonium ion mechanism.

Reaction of Olefins with Acetylacetone in the Presence of Thallic Acetate. K. Ichikawa, S. Uemura and T. Sugita. *Tetrahedron* **22**, 407 (1966).—In acetic acid solution containing thallic acetate and perchloric acid, ethylene reacts with acetylacetone to give 3-acetyl-2-methyl-4,5-dihydrofuran as the major product. Similarly, styrene gives 3-acetyl-2-methyl-4-phenyl-4,5-dihydrofuran. Formation of these products can be explained by a mechanism through a reaction between olefin-thallic acetate addition compounds and active methylene of acetylacetone.

Iodo-Demercuration of Phenylmercuric Compounds. Osamu Itoh, Hisashi Taniguchi, Akira Kawabe and Katsuhiko Ichikawa. *Kogyo Kagaku Zasshi* **69**, 913 (1966) in Japanese.—The effects of substituents on the demercuration rates of phenylmercuric halides with iodine have been studied in a pyridine solution. The rates are second-order with respect to the mercurials and iodine. The relative rates of *p*-MeO-, *p*-Me-, *m*-Me-, H-, *m*-MeO-, *p*-Cl-, and *m*-Cl-C_6H_4HgBr at 0°C are

6.84, 2.78, 1.58, 1.00, 0.625, 0.094 and 0.059, respectively. Hammett plot of the rate constants against normal σ values gave a straight line with a ρ value of -2.87, showing that the reaction in a bimolecular electrophilic substitution. This result is interesting, because the Hammett plots of the similar reactions such as bromodeboronation of phenylboronic acids and bromonolysis of trimethylphenylsilanes to give benzene derivatives and bromo-trimethylsilane (both in acetic acid) are reported to give straight lines when σ^+ values are used. This discrepancy appears to have resulted from the effect of the solvent used. It is most likely that free carbonium ion (σ complex in aromatic substitution) is not formed during the course of the iodo-demercuration in pyridine because of the basicity of the solvent and the resonance stabilization of the carbonium ion cannot contribute to stabilize the intermediate. It is concluded that the reaction proceeds through S_E2 mechanism without forming carbonium ion intermediate.

Oxidation of Unsaturated Compounds with Thallic Acetate. Sakae Uemura, Ryohzoh Kitoh and Katsuhiko Ichikawa. *Nippon Kagaku Zasshi* **87**, 986 (1966), in Japanese.—Oxidation of various unsaturated compounds with thallic acetate in acetic acid is reported. The starting materials, being arranged in the order of decreasing reactivities, and the products (described in parentheses) are as follows: Isopropenyl acetate (acetone and acetoxyacetone), vinyl acetate (acetaldehyde, 1,1,2-triacetoxyethane and acetoxyacetaldehyde, propylene (1,2-diacetoxypropane), ethyl vinyl ether (acetaldehyde, 2-acetoxy-1,1-diethoxyethane and 1,2-diacetoxy-1-ethoxyethane), butadiene (3,4-diacetoxy-1-butene and monoacetate of 1-butene-3,4-diol), allyl acetate (1,2,3-triacetoxypropane), allyl chloride (1-chloro-2,3-diacetoxypropane and monoacetate of 1-chloro-2,3-propanediol), and ethylene (acetaldehyde and 1,2-piacetoxyethane). In ethanol the reaction is very slow and the results are as follows: Vinyl acetate (2-acetoxy-1,1-diethoxyethane and 1,1,2-triethoxyethane) and ethyl vinyl ether (2-acetoxy-1,1-diethoxyethane). When the strong acid is present (0.5mol./*l*), the reaction is very rapid, and the products are often different from those in the absence of the acid. The oxidation does not proceed with ω-bromostyrene, acrylonitrile and α,β-unsaturated carbonyl compounds. Catalytic actions of thallic salts have been observed for the addition of acetic acid to methyl vinyl ketone to yield 3-butanone-1-ol acetate and for the conversion of oxygen-substituted olefins to carbonyl compounds, *i.e.*, acetaldehyde formation from vinyl acetate and ethyl vinyl ether and acetone formation from isopropenyl acetate.

The Reaction of m-Xylene with Carbon Monoxide under Pressure. Yoshimasa Takezaki, Tadashi Teraoka, Nobuyuki Sugita, Hiroshi Teranishi and Kiyoshi Kubo. *Kogyo Kagaku Zasshi* **69**, 907 (1966), in Japanese.—Kinetic study has been made on the synthesis of 2,4-dimethylbenzaldehyde from *m*-Xylene-BF_3 complex and CO in hydrogen fluoride solution.

In the preliminary investigation, the relation has been obtained between BF_3 pressure and composition of the solution saturated with the complex $[(CH_3)_2C_6H_5^+ \cdot BF_4^-]$ which has been isolated by Olah et al. and is presumably present in the solution; the equilibrium constant of the complex formation has been found to be 53 (mole fraction unit) at 0°C.

As to the reaction of *m*-xylene with CO, the dissolution of CO into the liquid phase determines the rate at the concentration higher than 1/60 (charged molar ratio: *m*-X/HF), but the reaction in solution becomes rate-determining at a concentration below 1/60. The rate in the liquid phase is of the first order with regard to the dissolved CO and to the complex. The rate constant has been found to be 2.5×10^{-2} $(kg/cm^2)^{-1}\cdot min^{-1}$ at 0°C, and the activation energy 8 $kcal\cdot mol^{-1}$.

Hydrogen Fluoride-Catalyzed Addition of Carbon Monoxide to Propylene under High Pressures. Yoshimasa Takezaki, Yosio Fuchigami, Hiroshi Teranishi, Nobuyuki Sugita and Kiyoshi Kudo. *Bulletin of the Japan Petroleum Institute* 8, 31 (1966).—Isobutyric acid forming reaction of propylene with carbon monoxide has been studied in the presence of HF-H_2O catalyst under high pressures. The optimum conditions for the formation of acid have been decided as follows: water content of HF catalyst, 20 wt. %; charge ratio of HF to C_3H_6, 15 (mole ratio); reaction temperature, 94°C or lower; and the total pressure, 190kg/cm² or higher. Reaction temperature higher than 94°C is unfavorable because of accelerated polymerization of C_3H_6.

Reaction mechanism of the formation of isobutyric acid has been proposed, where the rate determining step,

$$C_3H_7^+ + CO \text{ (dissolved)} \longrightarrow C_3H_7CO^+,$$

being first-order with regard to each reactant. The rate expression for the yield of the acid has been derived and the apparent activation energy of the over-all reaction has been found to be 21.7kcal/mole.

The Reaction of Oxygen Atoms with Dimethyl Ether. Yoshimasa Takezaki, Sadayuki Mori and Hironobu Kawasaki. *Bulletin of the Chemical Society of Japan* **39**, 1643 (1966).—The gas-phase reaction of dimethyl ether with oxygen atoms produced by the mercury photosensitized decomposition of nitrous oxide has been studied by means of quantitative determinations of the reaction products. Characteristic products are water, methanol, formaldehyde, carbon monoxide, methoxyethanol and methyl formate. The possible mechanisms of the oxygen attack on the substrate have been considered, and the following steps postulated on the basis of the relative importance of these products and their time variations:

$$O + CH_3OCH_3 \xrightarrow{k_E} OH + CH_3OCH_2,\ OH + CH_3OCH_3 \longrightarrow H_2O + CH_3OCH_2$$
$$\text{and } CH_3OCH_2 + OH \longrightarrow CH_3O + CH_2OH.$$

The rate constant, k_E of the first step has been determined in the competitive reaction with *n*-butane as:

$$k_E = 6.3\times10^{10} \exp(-4700/RT) \text{ 1. } mol^{-1} \text{ } sec^{-1}.$$

Industries of CO Addition Reactions under High Pressure — Around the Reppe Reactions. (**Review**) Yoshimasa Takezaki. *Kagaku to Kogyo* **19**, 25 (1966), in Japanese.—Present status of the industry of organic syntheses with high pressure carbon monoxide is reviewed, in which attention is paid on the recent developments including the Reppe reactions.

In addition, some of the new reactions which appear to have potentiality to grow up to commercial scale are discussed.

Syntheses of Bis-Epoxy Compounds from Exo- and Endo-Norbornenecarboxylic Esters and Polymerization of the Epoxy Compounds. Tetsuo Hamada, Tatsuya Shono, Akira Oku and Ryohei Oda. *Kogyo Kagaku Zasshi* **69**, 2012 (1966), in Japanese.—The *exo*- and *endo*-isomers of norbornenecarboxylic acid were isolated from their mixture by iodolactonization method and some esters were synthesized from each isomer and aromatic dihydroxy compounds, such as hydroquinone, resorcinol, catechol or 2,2-*bis* (*p*-hydroxypenyl) propane.

Along with expected *endo-endo* ester, a mixed ester in which one acylcomponent is *endo*-isomer and another is *exo*-isomer was obtained from *endo*-norbornenecarboxylic acid and hydroquinone. The epoxidation of each ester was carried out in a mixture of ether and chloroform at room temperature by using monoperphthalic acid as an oxidizing agent. This peracid was the only one which gave pure epoxycompound. The polymerization of each epoxycompound was performed in a sealed tube at room temperature in the presence of triethylaluminum. The obtained polymers were soluble in dimethylformamide and *m*-cresol. The reduced viscosities of the polymers (up to 0.08), however, showed that the degree of polymerization was not so high as expected.

Syntheses of Bicyclo-lactone and -urethane Containing Cyclopropane Ring. Tatsuya Shono, Mamoru Narui, Akira Oku and Ryohei Oda. *Kogyo Kagaku Zasshi* **69**, 1488(1966), in Japanese.—*Cis*-1,2-cyclopropane dicarboxylic chloride was reduced with sodium borohydride to 2-keto-3-oxa-bicyclo [3.1.0]-hexane [I]. 1,2-Dimethylolcyclopropane was, however, obtained along with [I]. Similar reduction of cis-2-carbomethoxy-cyclopropanecarboxylic chloride gave I in a better yield. Like other five membered lactone, I did not polymerize. A cyclic urethane [V] was synthesized by Curtius method from the hydrazide, obtained from [I] and hydrazine hydrate. Furthermore, the trans-isomers were reduced in the same way as cis-isomers, and products were hydroxycarboxylic ester [VII], corresponding to [I], and polyurethane, corresponding to [V]. The inherent viscosity of the polyurethane was 0.23 and that of polyester obtained from [VII] was 0.14.

The Oxidation of Epoxides by Amine Oxides. Ryohei Oda, Yoshiyuki Hayashi and Takeshiro Yoshida. *Nippon Kagaku Zasshi* **87**, 975 (1966), in Japanese.— It is already known that keto-alcohol is the product of the reaction of epoxides with DMSO using BF_3 as catalyst. The similar reaction would be expected to occur by the reaction of epoxides with amineoxides, which have the same reactivity as DMSO. The authers have found, that keto-alcohol was obtained in a fairly good yield (46%) by the reaction of styreneoxide (I) with DMSO at 150°C (15hr) without the catalyst BF_3, and also cyclopentene-1-aldehyde (II) (yield, 3%) was obtained from cyclohexene oxide (III) and DMSO, besides the expected keto-alcohol.

In the reaction of epoxides with C_5H_5NO or $(CH_3)_3NO$, keto-alcohols were also obtained, but main products were the carbonyl compounds which were derived from the oxidative cleavage of the carbon-carbon chain of epoxide ring.

For example, the following products were identified : phenacyl alcohol (yield, 4~11%), benzaldehyde(4~47%)and HCHO from I ; 2-hydroxycyclohexanone (yield, 1~14%), II (yield, 3~17%) and a trace of adipaldehyde from III ; acetophenone (yield, 17%) and HCHO from α-methylstyreneoxide ; propionaldehyde (yield, 10%)

and paraformaldehyde (yield, 13%) from 1,2-butyleneoxide.

Stable Sulfur Ylids. Ryohei Oda and Yoshiyuki Hayashi. *Nippon Kagaku Zasshi* 87, 1110 (1966), in Japanese.—R. Gompper and H. Euchner have reported that stable sulfur ylids could be isolated from the reaction mixture of dimethylsulfoxide (DMSO), acetic anhydride and active methylene compounds.

The authors have also found that stable sulfur ylids were obtained from DMSO, acetic anhydride (or butyric anhydride) and active methylene compounds such as methyl acetoacetate, ethyl acetoacetate, ethyl benzoylacetate and acetylacetone in high yields.

These ylids were too stable to react with carbonyl compounds and also stable upon treatment with alkaline aqueous solutions but easily hydrolysed upon treatment with hot 1N sulfuric acid aqueous solution.

IR and NMR spectra of some ylids were discussed.

The Oxidation of Halides by Amine Oxides of Dimethyl Sulfoxide in the Presence of Epoxides. Ryohei Oda, Yoshiyuki Hayashi and Takeshiro Yoshida. *Nippon Kagaku Zasshi* 87, 978 (1966), in Japanese.—The oxidation of alkyl-and aralkyl-halides by amine oxides or sulfoxides is a remarkable selective oxidation.

In this reaction, the intermediates, that is alkoxyammonium salts or alkoxysulfonium salts, are decomposed by a base to carbonyl compounds.

The authors found that epoxides were very effective base in this oxidation. For example, benzaldehyde (yield, 82~87%) and α,α-dichloro isopropanol (yield, 62~66%) were obtained in the oxidation of benzylchloride by pyridine *N*-oxide (I) or DMSO in the presence of epichlorohydrin.

The oxidation of alkyl chlorides were difficult, while alkyl bromides were oxidized easily.

Chlorohydrins (yield, 22~41%) were isolated by the reaction of I with epoxides in ethylene dichloride.

Chlorohydrins derived from mono-substituted were mostly $RCH(OH)-CH_2Cl$. This result would suggest that epoxides eliminate halide anion from the bulky intermediates, that is, ammonium- or sulfonium-salts.

Epichlorohydrin was the most effective epoxide as halide anion acceptor.

The Reactions of Amide Chlorides with Grignard Reagents and $LiAlH_4$. Ryohei Oda, Seiichi Katsuragawa, Yoshihiko Ito and Masaya Okano. *Nippon Kagaku Zasshi* 87, 1236 (1966), in Japanese.—Nucleophilic substitutions of amide chlorides by Grignard reagents and $LiAlH_4$ have been investigated. In the reaction of simple amide chlorides with Grignard reagents, tertiary amines are generally obtained, together with aldehydes or ketones. These products correspond to compounds, which one or two chlorines of amide chlorides have been replaced by alkyl or aryl groups.

On the other hand, the Grignard reaction of *N,N'*-tetra-substituted and *N,N'*-disubstituted urea chlorides results in the formation of amides and amidines, which are derived from hydrolysis and dehydrochlorination of the monoalkylated intermediates, respectively.

In the reaction of simple amide chlorides with $LiAlH_4$, two chlorine atoms

are replaced by hydride ions yielding tertiary amines. The amide chloride-enamine and amide chloride Schiff base adducts, which correspond to a kind of bis-amide chlorides, are also reduced to the expected tetrasubstituted diamine.

Studies on the Syntheses of 1,2-Cyclopropanedicarboxaldehyde and 1,2-Diacetyl cyclopropane. Tatsuya Shono, Masatoshi Kimura, Akira Oku and Ryohei Oda. *Kogyo Kagaku Zasshi* **69**, 2147 (1966), in Japanese.—The syntheses of the 1,2-cyclopropanedicarboxaldehyde and 1,2-diacetylcyclopropane as the precursors of 1,2-divinylcyclopropane derivatives were studied. The *trans*-1, 2-cyclopropanedicarboxaldehyde was obtained by the reduction of *trans*-1, 2-cyclopropanedicarbonyl chloride with lithium tri-*tert*-butoxyaluminohydride or with Rosenmund reagent. The conversion of acid chloride to aldehyde was about 50% in both cases. Grignard reaction of *trans*-1,2-cyclopropanedicarbonitrile or *trans-N,N,N',N,'*-tetraethyl -1,2-cyclopropanedicarboxamide with methylmagnesium bromide was carried out to synthesize 1,2-diacetylcyclopropane, The reaction products isolated were, however, monoacetyl compounds, and this result indicates that only one of the original functional groups reacted with Grignard reagent. Furthermore, the reaction of *trans*-1,2-dibenzoylcyclopropane with Wadsworth reagent gave a monoolefinic product.

Sulfuric Acid Catalysed Reaction of Dimethylsulfoxide with Some Aromatic Compounds. Ryohei Oda and Yoshiyuki Hayashi. *Nippon Kagaku Zasshi* **87**, 291 (1966), in Japanese.—Methylsulfinylmethyl cation derived from dimethylsulfoxide (DMSO) and sulfuric acid was reacted with some aromatic compounds such as styrene, anisole and naphthalene to give methylsulfinylmethyl derivatives (I).

I was oxidised to sulfoxides by DMSO and the sulfoxides underwent Pummerer rearrangement to give aldehydes in the same medium.

Cinnamaldehyde, *o*- and *p*-methoxybenzaldehyde and α-naphthaldehyde were obtained from styrene, anisole and naphthalene respectively.

Methyl α-phenylethyl sulfide (II) was obtained in 12% yield by the reaction of styrene with dimethyl sulfide in sulfuric acid.

II and acetophenone were also obtained by the treatment of styrene with DMSO.

p,p'-Dimethoxydiphenylmethane, α,α'-dinaphthylmethane and methylenebisbenzamide were obtained by the jointing reaction of each aromatic compound with HCHO derived from the decomposition of DMSO by sulfuric acid.

Dimerization of styrene in DMSO or dimethyl sulfide in the presence of sulfuric acid yielded only 1,3-diphenyl butene-1.

The Effect of Inorganic Chlorides on the Amide Chloride-Epoxide Reaction. Ryohei Oda, Seiichi Katsuragawa, Yoshihiko Ito and Masaya Okano. *Nippon Kagaku Zasshi* 87, 490 (1966), in Japanese.—In the reaction of *N,N*-dimethylpropionamide chloride with propylene oxide, the yield and the ratio of two isomeric β-chloropropyl propionates were considerably affected by adding Lewis acids (*e. g.* $ZnCl_2$, $AlCl_3$, $TiCl_4$) and a neutra chloride (LiCl). An explanation for this effect is proposed.

Synthesis of 2-(p-Vinylphenyl) propylene Oxide and its Polymerization. Chi-

kahiko Nakashima, Shigeo Tanimoto and Ryohei Oda. *Kogyo Kagaku Zasshi* 68, 1726 (1965), in Japanese.—*p*-Vinylacetophenone and trimethylsulfonium iodide in dimethylsulfoxide were mixed with potassium tert-butoxide in dimethylsulfoxide at 20~25°C, under a nitrogen stream.

The reaction mixture was stirred for 2 hr, and added to a large volume of water, and an organic layer was separated. This layer was distilled in vacuo to obtain 55% 2-(*p*-vinylphenyl) propylene oxide (I) in 55% yield, bp 86~89°C/4.5 mmHg. I was also obtained by Grignard reaction; namely, chloroacetone was added to *p*-vinylphenylmagnesium chloride in tetrahydrofuran at 0°C, and the reaction mixture was stirred for 1~2 hr, followed by hydrolysis with 10% NH_4Cl aqueous solution. The organic layer was then poured dropwise into C_2H_5ONa in C_2H_5OH at -5~0°C. Water and ether were added to this mixture, and the organic layer was distilled in vacuo to obtain I in 11% yield, bp 83~86°C/3.5 mmHg.

I was polymerized in bulk at 70°C, using BPO as an initiator. The obtained polymer, having epoxy groups in a side chain, decomposed at 347°C, $[\eta]=0.70$ $dl\cdot g^{-1}$ (in benzene, at 30°C).

The crosslinked resin was obtained by heating I at 180°C, or heating I with ethylenediamine or adipic acid. These resins were hard and stable to acid and alkali, except H_2SO_4.

Also, I was an excellent adhesive for Al or glass.

Application of Ionic Telomers of Styrene with Methylene-bis-urethane. Yasuo Wada and Ryohei Oda. *Kogyo Kagaku Zasshi* 69, 361 (1966), in Japanese.—The ionic telomerization of styrene with methylene-*bis*-urethane has yielded α,ω-*bis*-urethanes containing from one to several styrene units, $H_5C_2OCONH\text{-}CH_2\text{-}(\text{-}CH_2\text{-}CHC_6H_5\text{-})_n\text{-}NHCOOC_2H_5$. The number of n is mainly 1 and 2. *N,N'-bis*-ethoxycarbonyl-1-phenylpropane-1,3-diamine ($n=1$) has been isolated by distillation, bp 183~190°C/3 mmHg. *N, N-bis*-ethoxycarbonyl-1, 3-diphenylpentamethylene-1, 5-diamine ($n=2$) has been saponified to 1,3-diphenylpentamethylenediamine. The diamine was identified by elemental analysis, IR spectra and was derived into *N,N'-bis*-phenylurea by reaction with phenylisocyanate.

The polycondensation of the telomers with hexamethylenediamine by heating under vacuum has yielded polyureas, $\text{-}[\text{-}NHCONH\text{-}CH_2\text{-}(CH_2CHC_6H_5)_n\text{-}NHCONH(CH_2)_6\text{-}]\text{-}_m$. The polyureas thus obtained are pale yellow powders, soluble in *m*-cresol and formic acid, and can be drawn into fiber. The polyurea from the telomer of $n=1$ has a melting range of 260~288°C and a $[\eta]$ of 0.27 (25°C, *m*-cresol).

On the other hand, reaction of the telomers with glycol in the presence of sodium ethylate has not yielded the expected polyurethane, but has yielded 4-phenyl-2-oxohexahydropyrimidine and low molecular weight polycondensation products.

The Preparation of Alkoxymethyl Acylates, the Intermediates of Polonovski Reaction. Yoshiyuki Hayashi and Ryohei Oda. *Nippon Kagaku Zasshi* 87, 627 (1966), in Japanese.—Alkoxymethyl acylates were obtained from Polonovski reaction of trimethylamine oxide with acetic anhydride in the presence of some alcohols.

This result substantiates the existence of the intermediate $(CH_3)_2N\text{-}CH_2\text{-}O\text{-}CO\text{-}CH_3$.

n-Butoxy-, cyclohexyloxy-, benzyloxy- and cinnamyloxy- methyl acetate were obtained in 26~69 % yields.

Cyclohexyloxymethyl butyrate and *n*-butoxymethyl benzoate were also obtained in poor yields.

Cyclohexyloxymethyl acetate was also isolated from the reaction mixture of *N*,*N*-dimethylaniline *N*-oxide, acetic anhydride and cyclohexanol.

Pyridine *N*-oxide catalysed the esterification of alcohols with acetic anhydride but very small amount of cyclohexanone (yield, 0.2 %) was obtained from the reaction mixture of pyridine *N*-oxide, acetic anhydride and cyclohexanol.

Novel Cyclo-oxidation of Biallyl. Iwao Tabushi and Ryohei Oda. *Tetrahehron Letters* **1966**, 2487.

The Mechanism of the Reaction of P-Ylides with Dichlorocarbene. Y. Ito, M. Okano and R. Oda. *Tetrahedron* **22**, 2615 (1966).—Relative rates of the reaction of ring-substituted α-carbethoxybenzylidenetriphenylphosphoranes with dichlorocarbene have been measured. The results and some information concerning the structural dependence of other P-ylides on yields strongly support a mechanism which involves a rate-determining attack of the carbene on a P-ylide followed by rapid elimination of a phosphine. In addition, the large differences in reactivity observed for fluorenylidene-, indenylidene- and cyclopentadienylidene-triphenylphosphorane could be explained from the relevant π-electron localization energies calculated by the simple LCAO-MO method.

A Synthesis of Jasmone. Keiiti Sisido, Yosiyuki Kawasima and Tyûzô Isida. *Perfumery and Essential Oil Record, London, June* **1966**, 3.—*cis*-Jasmone was synthesized from 5-methylfurfuryl alcohol prepared from cane sugar via new acetylenic compounds I, II, III and IV. *Trans*-Jasmone was found to be less stable than *cis*-jasmone.

Fragrant Flower Constituents of Osmanthus fragrans. Keiiti Sisido, Seizi Kurozumi, Kiitirô Utimoto and Tyûzô Isida. *Perfumery and Essential Oil Record*, London, September **1966**.—The fragrant constituents of the flowers of *Osmanthus fragrans* were determined as γ-decalactone, α- and β-ionone, *trans*- and *cis*-linaloöl oxides, linaloöl, pelargonic aldehyde, leaf alcohol, etc.

Diphenylmethylenecyclopropane. Keiiti Sisido and Kiitirô Utimoto. *Tetrahedron Letters* **1966**, 3267.

Stereochemistry of 1,2-Dimethyl-3-isopropylcyclopentane. Keiiti Sisido, Seizi Kurozumi, Kiitirô Utimoto, and Tyûzô Isida. *The Journal of Organic Chemistry* **31**, 2795 (1966).—(+)-1,*trans*-2-Dimethyl-*trans*-3-isopropylcyclopentane and (±)-1,*cis*-2-dimethyl-*trans*-3-isopropylcyclopentane were prepared from (+)-isoiridomyrmecin and (±)-dihydrophotocitral-A respectively. A mixture of stereoisomers of (+)-1,2-dimethyl-3-isopropylcyclopentanes was derived from crude (+)-iridodial. These products were compared with a mixture of stereoisomers of (±)-1,2-dimethyl-3-isopropylcyclopentanes synthesized from (±)-2-carbethoxy-5-methylcyclopentanone *via* (±)-1-methyl-2-methylene-3-isopropylcyclopentane. The stereochemistry of these syntheses is discussed.

Optical rotatory dispersion of rotundifolone. S. Shimizu, J. Katsuhara and Y. Inouye. *Agricultural and Biological Chemistry* **30**, 89 (1966).—The optical rotatory dispersion of rotundifolone and dihydro-rotundifolone was studied for the purpose of absolute assignment of configuration. The (1*S*:2*S*)-configuration of the naturally occurring (+)-rotundifolone (piperitenone oxide) deduced by ORD means was in agreement with that by chemical transformation and it was shown that the "reversed Octant rule" was applicable to this highly strained system.

The absolute configuration of *trans*-2-methylcyclopropanecarboxylic acid. T. Sugita and Y. Inouye. *Bulletin of the Chemical Society of Japan* **39**, 1075 (1966).—The stepwise transformation of (−)-(1*R*:2*R*)-*trans*-2-phenylcyclopropanecarboxylic acid into (−)-*trans*-2-methylcyclopropanecarboxylic acid (I) via intermediate compounds (−)-*trans*-hydroxymethyl-2-phenylcyclopropane (II) and (−)-*trans*-1-methyl-2-phenylcyclopropane (III), unequivocally established the absolute configurations of (I) as (−)-(1*R*:2*R*), (II) as (−)-(1*S*:2*R*) and (III) as (−)-(1*R*:2*R*).

Synthesis of (±)-hydroxytremetone. J. Oda, H. Fukami and M. Nakajima. *Agricultural and Biological Chemistry* **30**, 59 (1966).— (±)-Hydroxytremetone was synthesized from 2-(α-hydroxyisopropyl)-6-hydroxycoumaran via its 0-acetate by dehydration with phosphorus tribromide in pyridine, followed by acylation with a mixture of trifluoroacetic anhydride and acetic acid. Isohydroxytremetone was also synthesized.

The Structure and Total Synthesis of Takatonine. Seiju Kubota, Takehiko Masui, Eiichi Fujita, and S. Morris Kupchan. *The Journal of Organic Chemistry* **31**, 516 (1966).—Total syntheses of takatonine iodide and tetrahydrotakatonine by unequivocal routes show that takatonine iodide should be assigned the 1-(4′-methoxybenzyl)-5,6,7-trimethoxyisoquinoline methiodide structure, rather than the isomeric 6,7,8-trimethoxy structure considered earlier.

Terpenoids—II. The Chemical Conversion of Enmein into (−)-Kaurane—The Absolute Configuration of Enmein. E. Fujita, T. Fujita, K. Fuji, and N. Ito. *Tetrahedron* **22**, 3423 (1966).—The acyloin condensation of a lactone ester which was derived from enmein, a diterpenoid bitter principle from *Isodon trichocarpus* KUDO, afforded several products, the main compound of which was converted into (−)-kaurane through a series of reactions. On the basis of the result, the absolute configuration of enmein was positively established by a chemical evidence.

Isolation of Enmein and its 3-Acetate from *Isodon japonicus*. Eiichi Fujita, Tetsuro Fujita, and Masayuki Shibuya. *Chemical Communications*, **1966**, 297. Enmein and its 3-acetate were isolated from *Isodon japonicus* HARA. Enmein isolated from *I. trichocarpus* KUDO is usually contaminated with dihydroenmein. The n. m. r. spectrum of the enmein which was isolated from *I. japonicus*, however, showed it to be pure.

Diterpenoid Constituents of *Isodon trichocarpus* and *Isodon japonicus* (Terpenoids IV). Eiichi Fujita, Tetsuro Fujita, and Masayuki Shibuya. *Tetrahedron Letters*, **1966**, 3153.—Six kinds of new diterpenoids—isodocarpin, nodosin, isodotricin, trichodonin, ponicidin, and oridonin—have been isolated from *Isodon trichocarpus*

KUDO and *Isodon japonicus* HARA. The structure of isodocarpin has been established as 3-desoxyenmein. Nodosin has proved to have the structure corresponding to 11-β-hydroxyisodocarpin. The structure of 17-methoxy-16-*epi*-dihydroenmein has been proposed for isodotricin.

Tumor Inhibitors. XV. The Structure and Configuration of Cissampareine, a Novel Bisbenzylisoquinoline Alkaloid. S. Morris Kupchan, S. Kubota, E. Fujita, S. Kobayashi, J. H. Block, and S. A. Telang. *Journal of the American Chemical Society* 88, 4212 (1966).—Elemental analysis and molecular weight determination by mass spectrometry supported a $C_{37}H_{38}N_2O_6$ molecular formula for cissampareine. Functional group analysis and spectral evidence showed the presence of three O-methyl groups and one N-methyl group, a hindered phenolic hydroxyl group, and a 3,4-dihydroisoquinoline partial structure. Sodium in liquid ammonia reduction of O-methylcissampareine yielded a levorotatory nonphenolic base and a dextrorotatory phenolic base. The nonphenoli base proved to have the structure 1-(4′-methylbenzyl)-2-methyl-6,7-dimethoxy-1, 2, 3, 4-tetrahydroisoquinoline by its n.m.r. and o.r.d. spectral characteristics, by its oxidation to 1-oxo-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline, and by direct comparison with a racemic sample prepared by total synthesis The phenolic base was shown to have the structure 1-(4′-hydroxybenzyl)-7-hydroxy-6, 8-dimethoxy-1, 2, 3, 4-tetrahydroisoquinoline by methylation, by its negative Gibbs test, and by comparison with a sample prepared by total synthesis. Sodium in liquid ammonia reduction of O-ethylcissampareine indicated that the phenolic hydroxy group is located in the benzyl-3,4-dihydroisoquinoline moiety of cissampareine. Thus, the structure and configuration were assigned to the alkaloid.

Alkaloids of *Hernandia ovigera*: the Characterization and Structures of Five New Aporphine Bases. M. P. Cava, K. Bessho, B. Douglous, S. Markey, R. F. Raffauf, and J. A. Weisbach. *Tetrahedron Letters.* **1966**, 1577.—In addition to thalicarpine and isocorydine, five new alkaloids were isolated from *Hernandia ovigera* and their structures were elucidated.

Hernandia Alkaloids. II. Hernandaline, a New, Elaborated Aporphine Structural Type.—M. P. Cava, K. Bessho, B. Douglous, S. Markey, and J. A. Weisbach. *Tetrahedron Letters.* **1966**, 4279.—From *Hernandia ovigera* were further isolated three compounds; laurotetanine, N-methyl-6,7-dimethoxyisoquinolone and hernandaline. The structure of hernandaline was proposed by spectral studies and established by synthesis. Isolation of isocorydine, hernovine, ovigerine, N-methylovigerine, N-methylnandigerine, nandigerine, norisocorydine, O,O-dimethylcorytuberine, N-methyllaurotetanine, laurolitsine, and a new alkaloid catalipifoline from *Hernandia catalipifolia* was also reported.

New characteristic alpha-amylase in sweet potatoes. Masayuki Ikemiya and H. J. Deobald. *Journal of Agricultural and Food Chemistry* 44, 237 (1966).—A new amylolytic enzyme has been demonstrated in raw sweet potato juice. Its dextrinizing activity places it with the α-amylases. Among its unusual characteristics were high optimum activity temperature, heat stability, and low activity at ordinary temperatures. The optimum temperature was 70° to 75°C. The enzyme

showed maximum resistance to heat inactivation at pH 6.0, while a much wider range of pH (3.6 to 8.1) was tolerated vested sweet potatoes contain relatively small amounts of this enzyme, which increases about sixfold after 9 months' storage. Unlike the sweet potato β-amylase, this enzyme is distributed almost uniformly throughout the inner tissues of the root and is more soluble in water than in sweet potato juice.

L-Lysine-α-ketoglutaric acid transaminase. Kenji Soda, Haruo Misono and Tatsuo Yomamoto. *Symposium on Enzyme Chemistry*, **18**, 316 (1966).—The properties of the reaction product and the purified transaminase from *Flavobacterium fuscum* were investigated. The formation of the bisulfite adduct of α-aminoadipic-δ-semialdehyde produced from L-lysine and of the dimer of Δ'-piperideine-6-carboxylic acid (tetrahydroanabasine dicarboxylic acid) was demonstrated.

Reduction of polylysyl soluble RNA to polylysyl lysinol by lithium borohydride. Kenji Soda, Sara Jo Marble, Norman W. Coles and Alton Meister. *Biochimica et Biophysica Acta* **103**, 534 (1966).—The aminoacyl s-RNA fraction obtained in the polyadenylic acid-stimulated reaction was treated with $LiBH_4$, and evidence was obtained for the formation of free lysinol as well as polylysyl lysinol. Under these conditions, $LiBH_4$ acts on the ester linkage and has no appreciable action on peptide bends.

Metabolism of L-theanine, D-theanine and the related compounds in bacteria, Part I. Bacterial and enzymatic hydrolysis of L- and D-isomers of theanine and identification of products. Kenji Soda, Kazuko Uchiyama and Koichi Ogata. *Agricultural and Biological Chemistry* **30**, 541 (1966).—Some strains of *Pseudomonas* was found capable of utilizing L-theanine or D-theanine as a sole nitrogen and carbon source. The cell-free extract catalyzes the hydrolysis of the amide group of the compounds and the hydrolase activity was influenced remarkably by the nitrogen source in the medium. L-Theanine and D-theanine were hydrolyzed to yield stoichiometrically L-glutamic acid and D-glutamic acid, respectively, and ethylamine, which were isolated from the reaction mixture and identified.

Metabolism of L-theanine, D-theanine and the related compounds in bacteria, Part II. Purification and properties of the enzyme hydrolyzing L-theanine, D-theanine and the related compounds. Kenji Soda, Kazuko Uchiyama and Koichi Ogata. *Agricultural and Biological Chemistry* **30**, 547 (1966).—The theanine hydrolase of *Pseudomonas aeruginosa* was purified approximately 200-fold. It was shown that the activities of L-theanine hydrolase, D-theanine hydrolase and the heat-stable L-glutamine hydrolase and D-glutamine hydrolase are ascribed to a single enzyme, which may be regarded as a γ-glutamyltransferase from the point of view of the substrate specificity and the properties. This theanine hydrolase catalyzed the transfer of γ-glutamyl moiety of the substrates and glutathione to hydroxylamine. L-Glutamine and D-glutamine were hydrolyzed by the theanine hydrolase and also by the heatlabile enzyme of the same strain of *Pseudomonas aeruginosa*, whose properties resembled the common glutaminase.

L-Lysine-α-ketoglutaric acid transaminase reaction : Identification of the product from L-lysine. Kenji Soda, Haruo Misono and Tatsuo Yamamoto. *Agricul-*

tural and Biological Chemistry **30**, 944 (1966).—Transaminase activity between L-lysine and α-Ketoglutaric acid was confirmed to be present in the cell-free extracts of *Flavobacterium fuscum*, *Fl. flavescens* and *Achromobacter liquidum*. The product from L-lysine was isolated from the reaction mixture by ion exchanger column chromatography, and identified as *Δ'*-piperideine-6-carboxylic acid, which is formed from α-aminoadipic-δ-semialdehyde by an intramolecular dehydration. The latter compound is derived direct from L-lysine by the transaminase reaction. Some properties of the enzyme were investigated.

Studies on enzymatic hydrolysis of theanine and the related compounds. Kenji Soda, Kazuko Uchiyama and Koichi Ogata. *Amino Acids and Nucleic Acids* **14**, (1966) in press. (in Japanese).—Microbial and enzymatic hydrolysis of L-theanine, D-theanine and other γ-glutamyl compounds, and enzymatic transfer reaction of γ-glutamyl group to hydroxylamine were reviewed and discussed.

Petroleum microbiology. Tatsuo Yamamoto and Takaharu Osumi. *Journal of Japan Petroleum Institute* **9**, 40 (1966), in Japanese.—Microbial purification of petroleum, microbial production of fatty acids, amino acids and other useful organic compounds from petroleum, and microbial metabolism of hydrocarbons in petroleum were reviewed.